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Absorption and Light Scattering in Insulators[1])

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Abstract. The interaction between electromagnetic radiation, lattice vibrations and excitons in insulating crystals has been studied by means of the Green's function technique. The spectral functions for the three fields have been derived and are found to be made, in the presence of anharmonic interactions, of the superposition of a Lorentzian line and an asymmetric band. Asymmetry is present even if the frequency dependence of the damping function is ignored. The scattering probability is examined for various kinds of coupling functions and it is found that no divergence occurs under resonance conditions.

I. Introduction

The aim of the present study is the theoretical investigation of the absorption and scattering of light in insulating crystals, with emphasis on the line-shape of the absorption bands and on the Raman effect under resonance conditions. Raman scattering experiments with the exciting frequency in a resonance region have been reported for large-gap semiconductors, mostly II-VI and III-V compounds [1], where the incident laser light approaches the absorption edge.

A theoretical treatment of the first- and second-order Raman effects in insulating solids has been presented by Loudon [2], which is based on a time-dependent Rayleigh–Schrödinger perturbation theory. Loudon has shown that the dominant contribution to the Raman effect arises from a process in which an electron-hole pair is excited by the incident photon; then the electron-lattice interaction leads to the scattering of the electron and hole by photons and the pair finally recombine to give the outgoing photon. Loudon [2] has not discussed explicitly the effect of Coulomb interaction between the excited electron and hole on the frequency dependence of the scattering efficiency S. He found that, when this last interaction is ignored, the scattering efficiency S does not diverge when the excitation energy $\hbar\omega$ is equal to the energy gap E_g, even though the energy denominators coming from perturbation theory vanish, because the density of excited states vanishes as $\hbar\omega$ approaches E_g.

Birman and Ganguly [3] have argued that the Coulomb interaction has to be considered in order to discuss the frequency dependence of S in resonant conditions. This interaction gives rise to the formation of excitons, the excitation energy of which is smaller than E_g. When excitons are included as intermediate states in Loudon's

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expression, one gets a sum over discrete exciton bound states; the energy denominators in this sum vanish as $\hbar\omega$ approaches an excitonic level and thus, Birman and Ganguly [3] have claimed that the excitonic part of the scattering efficiency diverges under resonance conditions. Like Loudon [2], Birman and Ganguly [3] have considered the Raman effect as arising from the absorption of the incident photon with the creation of an exciton, scattering of the exciton by phonons and recombination of the pair with emission of the outgoing photon, with different time ordering of these events. The interaction between the electrons and the electromagnetic radiation has again been treated through perturbation theory, which does not cover the resonance conditions.

Mills and Burstein [4] have pointed out that the electromagnetic radiation can be coupled strongly to the electric-dipole excitations in the crystal. When the photon frequency is close to a resonance in the dielectric constant, a large fraction of the energy of the propagating wave is contained in the dipolar excitations that dress the photon. These mixed modes made of an electromagnetic wave clothed by dipolar excitations are called polaritons. Mills and Burstein [4] have considered the Raman effect as the inelastic scattering of a propagating polariton by the lattice vibrations of the crystal, which is of particular importance under resonance conditions. They have shown that the divergent denominators, which appear in Birman and Ganguly's results [3], are replaced by the difference between polariton energies associated with different branches which never cross, so that S does not diverge. In a similar fashion, one can say that as the excitation frequency $\hbar\omega$ approaches an exciton energy $E_{\mathbf{k}\lambda}$, the $\mathbf{k}\lambda$-exciton content of the polariton increases until the mode is a pure $\mathbf{k}\lambda$-exciton for $\hbar\omega = E_{\mathbf{k}\lambda}$, without participation from the other exciton states or from the photon field; this is equivalent to say that the first-order exciton-photon interaction vanishes. Thus, while the energy difference in the denominator goes to zero, the corresponding oscillator strength in the numerator also vanishes leading to a finite, non-divergent result.

In fact, not only the electromagnetic and exciton fields can interact strongly but also the exciton-phonon interaction may become substantial, especially in the presence of polar longitudinal optical (LO) phonons in a non-centrosymmetric crystal. Hence, the polariton-phonon system, which has been treated within the framework of perturbation theory in the above-mentioned studies, can be formulated in such a way that the three fields, electromagnetic, exciton and phonon, are treated on the same footing. The propagating mode is then a dressed polariton consisting of an admixture of the three interacting fields and the Raman effect is considered as the dressed polariton-polariton inelastic scattering process.

Our approach to the problem starts from the same model Hamiltonian as that used by Ganguly and Birman [3], to which anharmonic terms have been added, describing photon-phonon and exciton-phonon interactions and is presented in Section II. Expressions for the Green functions of the coupled exciton, photon and phonon fields are derived in Section III through Dyson's equation. In Section IV, the excitation spectrum of the system is analysed in successive approximations. When all anharmonic effects are discarded the excitation spectrum is considered in the static approximation. In this approximation, the spectrum consists of dressed (by the phonon field) polariton modes which propagate through the crystal independently. The exciton-phonon interaction modifies the oscillator strength for the electronic transition in question and shifts the dispersion energies determined by the solutions of the Maxwell equations. In Section V, the dynamic corrections arising from anharmonicity are included and the polarization operator is calculated in the representation which is correct in the static approximation. The spectral functions corresponding to the three fields are derived and the absorption lines are found to consist of the superposition of Lorentzian lines peaked at the roots of the particular secular equation and of asymmetric lines, which describe the structure of the side bands. Asymmetric broadening of the main line may also arise when the energy dependence of the damping function is considered. The asymmetric broadening of the spectral lines is always present and is caused by anharmonic polariton interactions.

In Section VI, an expression for the scattering probability is derived in the dressed polariton representation. It is shown that no divergence appears under resonance conditions and the exciton-phonon interaction brings in a shift in the resonance energy as well as an additional contribution to the scattering amplitude. When this coupling is ignored, the expression for the polariton-phonon scattering amplitude is found to be in agreement with the results of Mills and Burstein [4]. The Raman scattering probability is also considered when the three fields are independent of one another. Physical processes that occur when either the three fields are coupled or the two fields are coupled and the other is independent have been discussed in detail.

II. Form of the Hamiltonian

Let us consider an insulator or a large gap semiconductor containing two or more atoms per unit cell. To study the behaviour of the system, where three fields: exciton, phonon and photon interact, we take the model Hamiltonian H as [3]

$$H = H^0 + H^1 + H^2 + H^3, \tag{2.1}$$

where H_0 consists of the unperturbed Hamiltonians

$$H^0 = H^0_{ex} + H^0_L + H^0_R, \tag{2.2a}$$

corresponding to the free exciton, phonon and photon fields respectively and given by

$$H^0_{ex} = \sum_{\mathbf{k}\lambda cv} E_{\mathbf{k}\lambda}(cv)\, \alpha^\dagger_{\mathbf{k}\lambda}(cv)\, \alpha_{\mathbf{k}\lambda}(cv) \tag{2.2b}$$

$$H^0_L = \sum_{\eta\xi} \omega_{\eta\xi}(b^\dagger_{\eta\xi} b_{\eta\xi} + \tfrac{1}{2}) \tag{2.2c}$$

$$H^0_R = \sum_{\chi\epsilon} \omega_{\chi\epsilon}(A^\dagger_{\chi\epsilon} A_{\chi\epsilon} + \tfrac{1}{2}) + \frac{\omega_p^2}{4} \sum_{\chi\epsilon} \frac{1}{\omega_{\chi\epsilon}} \bar{A}^\dagger_{\chi\epsilon} \bar{A}_{\chi\epsilon}. \tag{2.2d}$$

An exciton is defined as an electron-hole pair, where an electron in the conduction band c and a hole in the valence band v are bound together through the Coulomb interaction [5]. $\alpha^\dagger_{\mathbf{k}\lambda}(cv)$ and $\alpha_{\mathbf{k}\lambda}(cv)$ are the exciton creation and annihilation operators with wave-vector $\mathbf{k}$ and internal quantum number λ. $b^\dagger_{\eta\xi}$, $b_{\eta\xi}$ and $A^\dagger_{\chi\epsilon}$, $A_{\chi\epsilon}$ are the creation and annihilation operators for the phonon and transverse photon fields with wave-vectors $\boldsymbol{\eta}$ and $\boldsymbol{\chi}$ and polarization ξ and ϵ respectively, and satisfy Bose statistics. $E_{\mathbf{k}\lambda}(cv)$, $\omega_{\eta\xi}$ and $\omega_{\chi\epsilon}$ denote the energy for the exciton, phonon and photon fields respectively. The last term in (2.2d) represents the static part of the electron-photon interaction, which is proportional to the square of the vector potential [6] and ω_p is the plasma frequency. Explicit expressions for $E_{\mathbf{k}\lambda}(cv)$ are given in Reference [3]. Following Birman and Ganguly [3], we shall assume that the exciton operators satisfy Bose commutation relations. The band indices c and v will be suppressed into the compound index λ, for convenience, and the system of units, where $\hbar = 1$ will be used throughout. In Equations (2.2) use has been made of the following notation:

$$\bar{A}_{\chi\epsilon} = A_{\chi\epsilon} + A^{\dagger}_{-\chi\epsilon}, \quad \tilde{A}_{\chi\epsilon} = A_{\chi\epsilon} - A_{-\chi\epsilon}$$
$$\bar{b}_{\eta\xi} = b_{\eta\xi} + b^{\dagger}_{-\eta\xi}, \quad \tilde{b}_{\eta\xi} = b_{\eta\xi} - b^{\dagger}_{-\eta\xi}$$
$$\bar{\alpha}_{\mathbf{k}\lambda} = \alpha_{\mathbf{k}\lambda} + \alpha^{\dagger}_{-\mathbf{k}\lambda}, \quad \tilde{\alpha}_{\mathbf{k}\lambda} = \alpha_{\mathbf{k}\lambda} - \alpha^{\dagger}_{-\mathbf{k}\lambda}.$$

The first-order Hamiltonian H^1 can be written as

$$H^1 = H^1_{eL} + H^1_{eR}, \tag{2.3a}$$

where the bilinear interaction terms are given by

$$H^1_{eL} = \sum_{\substack{\mathbf{k}\lambda \\ \eta\xi}} g_{\eta\xi}(\mathbf{k}\lambda)\, \delta_{\mathbf{k},-\eta}\, \tilde{\alpha}^{\dagger}_{\mathbf{k}\lambda} \bar{b}_{\eta\xi}, \tag{2.3b}$$

$$H^1_{eR} = \sum_{\substack{\mathbf{k}\lambda \\ \chi\epsilon}} f_{\chi\epsilon}(\mathbf{k}\lambda)\, \delta_{\mathbf{k},-\chi}\, \tilde{\alpha}^{\dagger}_{\mathbf{k}\lambda} \bar{A}_{\chi\epsilon}. \tag{2.3c}$$

H^1_{eL} and H^1_{eR} represent physical processes, where either an exciton or a photon is created or annihilated through the absorption or emission of a phonon respectively. The coupling functions can be obtained by using Toyozawa's [7] procedure and are given in Ganguly and Birman's paper [**3**].

Similarly, the cubic and quartic anharmonicities, H^2 and H^3, are given by:

$$H^2 = H^2_{eeL} + H^2_{eLL} + H^2_{eeR} + H^2_{eRL} + H^2_{RRL}, \tag{2.4a}$$

$$H^3 = H^3_{eeLL} + H^3_{eRLL}. \tag{2.5a}$$

The specific form of the interaction terms is the following:

$$H^2_{eeL} = \sum_{\substack{\mathbf{k}\lambda\mathbf{k}'\lambda' \\ \eta\xi}} G_{\eta\xi}(\mathbf{k}\lambda, \mathbf{k}'\lambda')\, \delta_{\mathbf{k}-\mathbf{k}',-\eta}\, \alpha^{\dagger}_{\mathbf{k}\lambda} \alpha_{\mathbf{k}'\lambda'} \bar{b}_{\eta\xi}, \tag{2.4b}$$

$$H^2_{eLL} = \sum_{\substack{\mathbf{k}\lambda \\ \eta\xi\eta'\xi'}} d_{\eta\xi\eta'\xi'}(\mathbf{k}\lambda)\, \delta_{\eta+\eta'-\mathbf{k}}\, \tilde{\alpha}^{\dagger}_{\mathbf{k}\lambda} \bar{b}_{\eta\xi} \bar{b}_{\eta'\xi'}, \tag{2.4c}$$

$$\begin{aligned} H^2_{eeR} = \sum_{\substack{\mathbf{k}\lambda\mathbf{k}'\lambda' \\ \chi\epsilon}} [F_{\chi\epsilon}(\mathbf{k}\lambda, \mathbf{k}'\lambda')\, \delta_{\mathbf{k}-\mathbf{k}',-\chi}\, \alpha^{\dagger}_{\mathbf{k}\lambda} \alpha_{\mathbf{k}'\lambda'} \\ + F^{*}_{\chi\epsilon}(\mathbf{k}\lambda, \mathbf{k}'\lambda')\, \delta_{\mathbf{k}-\mathbf{k}',\chi}\, \alpha_{\mathbf{k}\lambda} \alpha^{\dagger}_{\mathbf{k}'\lambda'}]\, \bar{A}_{\chi\epsilon}, \end{aligned} \tag{2.4d}$$

$$H^2_{eRL} = \sum_{\substack{\mathbf{k}\lambda\chi\epsilon \\ \eta\xi}} \theta_{\eta\xi}(\mathbf{k}\lambda, \boldsymbol{\chi}\epsilon)\, \delta_{\mathbf{k},\chi+\eta}\, \tilde{\alpha}^{\dagger}_{\mathbf{k}\lambda} \bar{A}_{\chi\epsilon} \bar{b}_{\eta\xi}, \tag{2.4e}$$

$$H^2_{RRL} = \sum_{\substack{\chi\epsilon\chi'\epsilon' \\ \eta\xi}} \phi_{\eta\xi}(\chi\epsilon, \chi'\epsilon')\delta_{\chi-\chi',-\eta} \bar{A}^{\dagger}_{\chi\epsilon} \bar{A}_{\chi'\epsilon'} \bar{b}_{\eta\xi}, \tag{2.4f}$$

$$H^3_{eeLL} = \sum_{\substack{\mathbf{k}\lambda\mathbf{k}'\lambda' \\ \eta\xi\eta'\xi'}} D_{\eta\xi\eta'\xi'}(\mathbf{k}\lambda, \mathbf{k}'\lambda')\, \delta_{\mathbf{k}'-\mathbf{k},\eta+\eta'}\, \alpha^{\dagger}_{\mathbf{k}\lambda} \alpha_{\mathbf{k}'\lambda'} \bar{b}_{\eta\xi} \bar{b}_{\eta'\xi'}, \tag{2.5b}$$

$$H^3_{eRLL} = \sum_{\substack{\mathbf{k}\lambda\chi\epsilon \\ \eta\xi\eta'\xi'}} \theta_{\eta\xi\eta'\xi'}(\mathbf{k}\lambda, \chi\epsilon)\, \delta_{\mathbf{k},\chi+\eta+\eta'}\, \tilde{\alpha}^{\dagger}_{\mathbf{k}\lambda} \bar{A}_{\chi\epsilon} \bar{b}_{\eta\xi} \bar{b}_{\eta'\xi'}. \tag{2.5c}$$

The expressions for H^2_{eeL}, H^2_{eeR} and H^3_{eeLL} describe physical processes, where two excitons scatter each other through the emission or absorption of one phonon, one photon and two phonons respectively. Similarly, the expressions for H^2_{eLL}, H^2_{eRL} and H^3_{eRLL} represent processes, where an exciton is either created or annihilated with the emission or absorption of two phonons, one photon and one phonon, and one photon and two phonons respectively. Photon-photon scattering through the emission or absorption of a phonon is described by the expression H^2_{RRL}. All these anharmonic interactions will contribute to the lifetime and broadening of the spectral lines. It is easily seen that the expressions for H^2_{eeR}, H^2_{eRL}, H^2_{RRL} and H^3_{eLLL} describe direct photon scattering processes. The various coupling functions in Equations (2.4) and (2.5) can be found in the works of Ganguly and Birman [3] and Mavroyannis and Pathak [8]. It is pointed out that in addition to the exciton-lattice interaction via the deformation potential [9], there is the Fröhlich [10] interaction between excitons and LO phonons in polar crystals, which contributes to H^1_{eL}, H^2_{eeL}, H^2_{eLL}, H^2_{eRL} and to the quartic anharmonic terms (2.5). This contribution can be large and cannot be neglected particularly for polar crystals.

III. Green's Functions Derivation

To study the system made of three coupled fields, we will use the Green's function technique as described by Zubarev [11]. Let us introduce the following row operators

$$\bar{B}_k^\dagger = (\alpha^\dagger_{\mathbf{k}\lambda}\ \bar{A}^\dagger_{\mathbf{k}\epsilon}\ \bar{b}^\dagger_{\mathbf{k}\xi}\ \alpha_{-\mathbf{k}\lambda}) \tag{3.1a}$$

$$\tilde{B}_{\mathbf{k}}^\dagger = (\alpha^\dagger_{\mathbf{k}\lambda}\ \tilde{A}^\dagger_{\mathbf{k}\epsilon}\ \tilde{b}^\dagger_{\mathbf{k}\xi}\ \alpha_{-\mathbf{k}\lambda}) \tag{3.1b}$$

defined in terms of the exciton, photon and phonon operators. Using these operators together with their complex conjugate-column operators, we define the two double-time retarded Green's functions in matrix form

$$\langle\langle \bar{B}_{\mathbf{k}}(t)\,;\bar{B}^\dagger_{\mathbf{k}}(t')\rangle\rangle = -i\theta(t-t')\langle[\bar{B}_{\mathbf{k}}(t),\ \bar{B}^\dagger_{\mathbf{k}}(t')]_-\rangle \tag{3.2a}$$

$$\langle\langle \tilde{B}_{\mathbf{k}}(t)\,;\bar{B}^\dagger_{\mathbf{k}}(t')\rangle\rangle = -i\theta(t-t')\langle[\tilde{B}_{\mathbf{k}}(t),\ \bar{B}^\dagger_{\mathbf{k}}(t')]_-\rangle. \tag{3.2b}$$

The angular brackets denote that the statistical average of the commutator is taken over the canonical ensemble appropriate to the total Hamiltonian H; $\theta(t)$ is the usual Heavyside step function. The operators $\bar{B}_{\mathbf{k}}(t)$, $\tilde{B}_{\mathbf{k}}(t)$ are in the Heisenberg representation

$$B_{\mathbf{k}}(t) = \exp(iHt)\ B_{\mathbf{k}}(o)\exp(-iHt). \tag{3.3}$$

The equations of motion for the Fourier transforms of the Green's functions (3.2) with respect to the time argument t are given by [11]

$$\omega\langle\langle\bar{B}_{\mathbf{k}};\bar{B}^\dagger_{\mathbf{k}}\rangle\rangle = \frac{1}{2\pi}\langle[\bar{B}_{\mathbf{k}},\bar{B}^\dagger_{\mathbf{k}}]_-\rangle_{t=t'} + \langle\langle[\bar{B}_{\mathbf{k}},H]_-;\bar{B}^\dagger_{\mathbf{k}}\rangle\rangle \tag{3.4a}$$

$$\omega\langle\langle\tilde{B}_{\mathbf{k}};\bar{B}^\dagger_{\mathbf{k}}\rangle\rangle = \frac{1}{2\pi}\langle[\tilde{B}_{\mathbf{k}},\bar{B}^\dagger_{\mathbf{k}}]_-\rangle_{t=t'} + \langle\langle[\tilde{B}_{\mathbf{k}},H]_-;\bar{B}^\dagger_{\mathbf{k}}\rangle\rangle. \tag{3.4b}$$

When the commutator in the last two terms of Equations (3.4) is considered, the equations of motion (3.4) are coupled. Therefore, it is convenient to write Equations

(3.4) in the form of a linear combination, i.e.,

$$\omega[\Omega\langle\langle \bar{B}_{\mathbf{k}}\,;\bar{B}_{\mathbf{k}}^{\dagger}\rangle\rangle + \Omega_{\mathbf{k}}\langle\langle \tilde{B}_{\mathbf{k}}\,;\bar{B}_{\mathbf{k}}^{\dagger}\rangle\rangle]$$

$$= \frac{1}{2\pi}[\Omega\langle[\bar{B}_{\mathbf{k}},\bar{B}_{\mathbf{k}}^{\dagger}]_-\rangle_{t=t'} + \Omega_{\mathbf{k}}\langle[\tilde{B}_{\mathbf{k}},\bar{B}_{\mathbf{k}}^{\dagger}]_-\rangle_{t=t'}] \tag{3.5}$$

$$+ [\Omega\langle\langle[\bar{B}_{\mathbf{k}},H]_-\,;\bar{B}_{\mathbf{k}}^{\dagger}\rangle\rangle + \Omega_{\mathbf{k}}\langle\langle[\tilde{B}_{\mathbf{k}},H_-]\,;\;\bar{B}_{\mathbf{k}}^{\dagger}\rangle\rangle],$$

where the coefficients are given by:

$$\Omega = \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{\omega}{2} & 0 & 0 \\ 0 & 0 & \frac{\omega}{2} & 0 \\ 0 & 0 & 0 & \frac{1}{2} \end{pmatrix} \qquad \Omega_{\mathbf{k}} = \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{ck}{2} & 0 & 0 \\ 0 & 0 & \frac{\omega_{\mathbf{k}\xi}}{2} & 0 \\ 0 & 0 & 0 & \frac{1}{2} \end{pmatrix}. \tag{3.6}$$

When the commutators in (3.5) are calculated by means of the Hamiltonian (2.1), then the equation of motion (3.4a) takes the form of

$$D_{00}^{-1}(\mathbf{k},\omega)\langle\langle \bar{B}_{\mathbf{k}}\,;\bar{B}_{\mathbf{k}}^{\dagger}\rangle\rangle = I + \langle\langle S(\mathbf{k})\,;\bar{B}_{\mathbf{k}}^{\dagger}\rangle\rangle, \tag{3.7}$$

where I is the unit matrix. $D_{00}(\mathbf{k},\omega)$ is the unperturbed Green's function, which is found to be:

$$D_{00}^{-1}(\mathbf{k},\omega) = (2\pi)\begin{pmatrix} \omega - E_{\mathbf{k}\lambda} & -\sum_{\epsilon} f_{\mathbf{k}\epsilon}(\mathbf{k}\lambda) & -\sum_{\xi} g_{\mathbf{k}\epsilon}(\mathbf{k}\lambda) & 0 \\ -\sum_{\lambda} f_{\mathbf{k}\epsilon}^{*}(\mathbf{k}\lambda) & \dfrac{\omega^2 - c^2k^2 - \omega_p^2}{2ck} & 0 & \sum_{\lambda} f_{-\mathbf{k}\epsilon}^{*}(\mathbf{k}\lambda) \\ -\sum_{\lambda} g_{\mathbf{k}\xi}^{*}(\mathbf{k}\lambda) & 0 & \dfrac{\omega^2 - \omega_{\mathbf{k}\xi}^2}{2\omega_{\mathbf{k}\xi}} & \sum_{\lambda} g_{-\mathbf{k}\xi}^{*}(\mathbf{k}\lambda) \\ 0 & \sum_{\epsilon} f_{\mathbf{k}\epsilon}(\mathbf{k}\lambda) & \sum_{\xi} g_{\mathbf{k}\xi}(\mathbf{k}\lambda) & -\omega - E_{\mathbf{k}\lambda} \end{pmatrix} \tag{3.8}$$

In (3.7), $S(\mathbf{k})$ is a column operator arising from anharmonic contributions and is given by

$$S(\mathbf{k}) = \begin{pmatrix} S_{\mathrm{ex}}(\mathbf{k}) \\ S_R(\mathbf{k}) \\ S_L(\mathbf{k}) \\ S_{\mathrm{ex}}^{\dagger}(-\mathbf{k}) \end{pmatrix} = \begin{pmatrix} 2\pi[\alpha_{\mathbf{k}\lambda}, H^2 + H^3]_- \\ \pi[\tilde{A}_{\mathbf{k}\epsilon}, H^2 + H^3]_- \\ \pi[\tilde{b}_{\mathbf{k}\xi}, H^2 + H^3]_- \\ -2\pi[\alpha_{-\mathbf{k}\lambda}^{\dagger}, H^2 + H^3]_- \end{pmatrix}, \tag{3.9}$$

where the explicit expressions of its elements are:

$$S_{\mathrm{ex}}(\mathbf{k}) = 2\pi\Bigg\{\sum_{\substack{\mathbf{k}'\lambda'\\ \mathbf{k}''\xi''}} G_{\mathbf{k}''\xi''}(\mathbf{k}\lambda,\mathbf{k}'\lambda')\,\delta_{\mathbf{k}'-\mathbf{k}'',\mathbf{k}}\alpha_{\mathbf{k}'\lambda'}\bar{b}_{\mathbf{k}''\xi''} + \sum_{\substack{\mathbf{k}'\lambda'\\ \mathbf{k}''\epsilon''}} [F_{\mathbf{k}''\epsilon''}(\mathbf{k}\lambda,\mathbf{k}'\lambda')$$

$$+ F^{*}_{\mathbf{k}''\epsilon''}(\mathbf{k}'\lambda',\mathbf{k}\lambda)]\,\delta_{\mathbf{k}'+\mathbf{k}'',\mathbf{k}}\alpha_{\mathbf{k}'\lambda'}\bar{A}_{\mathbf{k}''\epsilon''} + \sum_{\substack{\mathbf{k}'\xi'\\ \mathbf{k}''\xi''}} d_{\mathbf{k}'\xi',\mathbf{k}''\xi''}(\mathbf{k}\lambda)\,\delta_{\mathbf{k}'+\mathbf{k}'',-\mathbf{k}}\bar{b}_{\mathbf{k}'\xi'}\bar{b}_{\mathbf{k}''\xi''}$$

$$+ \sum_{\substack{\mathbf{k}'\epsilon'\\ \mathbf{k}''\xi''}} \theta_{\mathbf{k}''\xi''}(\mathbf{k}\lambda,\mathbf{k}'\epsilon')\,\delta_{\mathbf{k}'+\mathbf{k}'',\mathbf{k}}\bar{A}_{\mathbf{k}'\epsilon'}\bar{b}_{\mathbf{k}''\xi''} + \sum_{\substack{\mathbf{k}'\lambda'\\ \mathbf{k}''\xi'',\mathbf{k}'''\xi'''}} D_{\mathbf{k}''\xi''\mathbf{k}'''\xi'''}(\mathbf{k}\lambda,\mathbf{k}'\lambda')$$

$$\times\,\delta_{\mathbf{k}'-\mathbf{k}''-\mathbf{k}''',\mathbf{k}}\alpha_{\mathbf{k}'\lambda'}\bar{b}_{\mathbf{k}''\xi''}\bar{b}_{\mathbf{k}'''\xi'''}$$

$$+ \sum_{\substack{\mathbf{k}'\epsilon'\\ \mathbf{k}''\xi''\mathbf{k}'''\xi'''}} \theta_{\mathbf{k}''\xi''\mathbf{k}'''\xi'''}(\mathbf{k}\lambda,\mathbf{k}'\epsilon')\,\delta_{\mathbf{k}'+\mathbf{k}''+\mathbf{k}''',\mathbf{k}}\bar{A}_{\mathbf{k}'\epsilon'}\bar{b}_{\mathbf{k}''\xi''}\bar{b}_{\mathbf{k}'''\xi'''}\Bigg\} \tag{3.10a}$$

$$S_R(\mathbf{k}) = 2\pi\Bigg\{\sum_{\substack{\mathbf{k}'\lambda'\\ \mathbf{k}''\lambda''}} \tfrac{1}{4}(F_{-\mathbf{k}\epsilon}(\mathbf{k}'\lambda',\mathbf{k}''\lambda'') + F^{*}_{-\mathbf{k}\epsilon}(\mathbf{k}''\lambda'',\mathbf{k}'\lambda')\,\delta_{\mathbf{k}'-\mathbf{k}'',-\mathbf{k}}(\bar{\alpha}^{\dagger}_{\mathbf{k}'\lambda'}\bar{\alpha}_{\mathbf{k}''\lambda''} + \tilde{\alpha}^{\dagger}_{\mathbf{k}'\lambda'}\tilde{\alpha}_{\mathbf{k}''\lambda''})$$

$$+ \sum_{\substack{\mathbf{k}'\lambda'\\ \mathbf{k}''\xi''}} \theta_{\mathbf{k}''\xi''}(\mathbf{k}'\lambda',-\mathbf{k}\epsilon)\,\delta_{\mathbf{k}'-\mathbf{k}'',-\mathbf{k}}\tilde{\alpha}^{\dagger}_{\mathbf{k}'\lambda'}\bar{b}_{\mathbf{k}''\xi''} + \sum_{\substack{\mathbf{k}'\epsilon'\\ \mathbf{k}''\xi''}} [\phi_{\mathbf{k}''\xi''}(\mathbf{k}'\epsilon',-\mathbf{k}\epsilon) + \phi_{\mathbf{k}''\xi''}(\mathbf{k}\epsilon,-\mathbf{k}'\epsilon')]$$

$$\times\,\delta_{\mathbf{k}'-\mathbf{k}'',-\mathbf{k}}\bar{A}_{\mathbf{k}'\epsilon'}\bar{b}_{\mathbf{k}''\xi''} + \sum_{\substack{\mathbf{k}'\lambda'\\ \mathbf{k}''\xi''\mathbf{k}'''\xi'''}} \theta_{\mathbf{k}''\xi''\mathbf{k}'''\xi'''}(\mathbf{k}'\lambda',-\mathbf{k}\epsilon)\,\delta_{\mathbf{k}'-\mathbf{k}''-\mathbf{k}''',-\mathbf{k}}\tilde{\alpha}^{\dagger}_{\mathbf{k}'\lambda'}\bar{b}_{\mathbf{k}''\xi''}\bar{b}_{\mathbf{k}'''\xi'''}\Bigg\} \tag{3.10b}$$

$$S_L(\mathbf{k}) = 2\pi\Bigg\{\sum_{\substack{\mathbf{k}'\lambda'\\ \mathbf{k}''\lambda''}} \tfrac{1}{4}G_{-\mathbf{k}\xi}(\mathbf{k}'\lambda',\mathbf{k}''\lambda'')\,\delta_{\mathbf{k}'-\mathbf{k}'',-\mathbf{k}}(\bar{\alpha}^{\dagger}_{\mathbf{k}'\lambda'}\bar{\alpha}_{\mathbf{k}''\lambda''} + \tilde{\alpha}^{\dagger}_{\mathbf{k}'\lambda'}\tilde{\alpha}_{\mathbf{k}''\lambda''})$$

$$+ \sum_{\substack{\mathbf{k}'\lambda'\\ \mathbf{k}''\xi''}} [d_{-\mathbf{k}\xi\mathbf{k}''\xi''}(\mathbf{k}'\lambda') + d_{\mathbf{k}''\xi''-\mathbf{k}\xi}(\mathbf{k}'\lambda')]\,\delta_{\mathbf{k}'-\mathbf{k}'',-\mathbf{k}}\tilde{\alpha}^{\dagger}_{\mathbf{k}'\lambda'}\bar{b}_{\mathbf{k}''\xi''}$$

$$+ \sum_{\substack{\mathbf{k}'\epsilon'\\ \mathbf{k}''\epsilon''}} \phi_{-\mathbf{k}\xi}(\mathbf{k}'\epsilon',\mathbf{k}''\epsilon'')\,\delta_{\mathbf{k}'-\mathbf{k}'',-\mathbf{k}}\bar{A}^{\dagger}_{\mathbf{k}'\epsilon'}\bar{A}_{\mathbf{k}''\epsilon''}$$

$$+ \sum_{\substack{\mathbf{k}'\lambda'\mathbf{k}''\lambda''\\ \mathbf{k}'''\xi'''}} \tfrac{1}{4}[D_{-\mathbf{k}\xi\mathbf{k}'''\xi'''}(\mathbf{k}'\lambda',\mathbf{k}''\lambda'') + D_{\mathbf{k}'''\xi'''-\mathbf{k}\xi}(\mathbf{k}'\lambda',\mathbf{k}''\lambda'')]\,\delta_{\mathbf{k}'-\mathbf{k}''-\mathbf{k}''',-\mathbf{k}}$$

$$\times\,(\bar{\alpha}^{\dagger}_{\mathbf{k}'\lambda'}\bar{\alpha}_{\mathbf{k}''\lambda''} + \tilde{\alpha}^{\dagger}_{\mathbf{k}'\lambda'}\tilde{\alpha}_{\mathbf{k}''\lambda''})\,\bar{b}_{\mathbf{k}'''\xi'''} + \sum_{\substack{\mathbf{k}'\lambda'\mathbf{k}''\epsilon''\\ \mathbf{k}'''\xi'''}} [\theta_{-\mathbf{k}\xi\mathbf{k}'''\xi'''}(\mathbf{k}'\lambda',\mathbf{k}''\epsilon'')$$

$$+ \theta_{\mathbf{k}'''\xi'''-\mathbf{k}\xi}(\mathbf{k}'\lambda',\mathbf{k}''\epsilon'')]\,\delta_{\mathbf{k}'-\mathbf{k}''-\mathbf{k}''',-\mathbf{k}}\tilde{\alpha}^{\dagger}_{\mathbf{k}'\lambda'}\bar{A}_{\mathbf{k}''\epsilon''}\bar{b}_{\mathbf{k}'''\xi'''}\Bigg\}. \tag{3.10c}$$

The second term on the right-hand side of (3.7) is a mixed many-particle Green's function, which can be written in a symmetric form by deriving its equation of motion with respect to the time argument t', together with that of the function $\langle\langle S(\mathbf{k});\tilde{B}^{\dagger}_{\mathbf{k}}\rangle\rangle$. Through a calculation similar to that used to obtain (3.7), we can write:

$$\langle\langle S(\mathbf{k});\bar{B}^{\dagger}_{\mathbf{k}}\rangle\rangle = [\langle[S(\mathbf{k}),B^{\dagger}_{\mathbf{k}}]_{-}\rangle_{t=t'} + \langle\langle S(\mathbf{k});S^{\dagger}(\mathbf{k})\rangle\rangle]\,D_{00}(\mathbf{k},\omega), \tag{3.11}$$

where the row vector appearing in the equal time commutator is defined as:

$$B_{\mathbf{k}}^{\dagger} = \left(\alpha_{\mathbf{k}\lambda}^{\dagger} \; \frac{\omega \bar{A}_{\mathbf{k}\epsilon}^{\dagger} + ck \tilde{A}_{\mathbf{k}\epsilon}^{\dagger}}{2ck} \; \frac{\omega \bar{b}_{\mathbf{k}\xi}^{\dagger} + \omega_{\mathbf{k}\xi}^{\dagger} \tilde{b}_{\mathbf{k}\xi}^{\dagger}}{2\omega_{\mathbf{k}\xi}} - \alpha_{-\mathbf{k}\lambda} \right) \tag{3.12}$$

and arises also from the linear combination of the two equations of motion for $\langle\langle S(\mathbf{k}); \bar{B}_{\mathbf{k}}^{\dagger}\rangle\rangle$ and $\langle\langle S(\mathbf{k}); \tilde{B}_{\mathbf{k}}^{\dagger}\rangle\rangle$.

Upon inserting (3.11) into (3.7), we obtain

$$\begin{aligned} D_{00}^{-1}(\mathbf{k},\omega)\langle\langle \bar{B}_{\mathbf{k}}^{\dagger}; \bar{B}_{\mathbf{k}}^{\dagger}\rangle\rangle &= D_{00}^{-1}(\mathbf{k},\omega)\, D(\mathbf{k},\omega) \\ &= I + [\langle [S(\mathbf{k}), B_{\mathbf{k}}^{\dagger}]_{-}\rangle_{t=t'} + \langle\langle S(\mathbf{k}); S^{\dagger}(\mathbf{k})\rangle\rangle]\, D_{00}(\mathbf{k},\omega), \end{aligned} \tag{3.13a}$$

which is to be compared with the Dyson equation

$$\begin{aligned} D_{00}^{-1}(\mathbf{k},\omega)\, D(\mathbf{k},\omega) &= I + \pi(\mathbf{k},\omega)\, D(\mathbf{k},\omega) \\ &= I + \bar{P}(\mathbf{k},\omega)\, D_{00}(\mathbf{k},\omega) \end{aligned} \tag{3.13b}$$

The polarization operator $\pi(\mathbf{k},\omega)$ is related to the scattering operator $\bar{P}(\mathbf{k},\omega)$ through

$$\begin{aligned} \pi(\mathbf{k},\omega) &= \bar{P}(\mathbf{k},\omega)[I + D_{00}(\mathbf{k},\omega)\, \bar{P}(\mathbf{k},\omega)]^{-1} \\ &= \bar{P}(\mathbf{k},\omega)[I - D_{00}(\mathbf{k},\omega)\, \bar{P}(\mathbf{k},\omega) \pm \ldots]. \end{aligned} \tag{3.14}$$

In the range of frequencies ω far from the zeros of the denominator in (3.14), we expand in power series and retain only the first term of the expansion. Using this approximation, from (3.13) we have

$$D(\mathbf{k},\omega) = [D_{00}^{-1}(\mathbf{k},\omega) - \langle [S(\mathbf{k}), B_{\mathbf{k}}^{\dagger}]_{-}\rangle_{t=t'} - \langle\langle S(\mathbf{k}); S^{\dagger}(\mathbf{k})\rangle\rangle]^{-1} I, \tag{3.15}$$

where the polarization operator $\pi(\mathbf{k},\omega)$ has been approximated by the scattering operator $\bar{P}(\mathbf{k},\omega) = \langle [S(\mathbf{k}), B_{\mathbf{k}}^{\dagger}]_{-}\rangle_{t=t'} + \langle\langle S(\mathbf{k}); S^{\dagger}(\mathbf{k})\rangle\rangle$. The equal time commutator is the static part of the scattering operator and is a renormalization term. The Green function $P(\mathbf{k},\omega) = \langle\langle S(\mathbf{k}); S^{\dagger}(\mathbf{k})\rangle\rangle$ is the dynamic component of $\bar{P}(\mathbf{k},\omega)$ and represents the effects of various scattering events among the particles arising from the anharmonic interactions $H^2 + H^3$.

Taking the diagonal and non-diagonal elements of (3.15), we obtain the following Green's functions for the exciton, photon and phonon fields:

$$\begin{aligned} D_{ex}(\mathbf{k},\omega) &= \langle\langle \tilde{\alpha}_{\mathbf{k}\lambda}; \tilde{\alpha}_{\mathbf{k}\lambda}^{\dagger}\rangle\rangle \\ &= \left(\frac{1}{\pi}\right) \cdot \frac{[\tilde{E}_{\mathbf{k}\lambda} + P_{14}(\mathbf{k},\omega)]}{[\omega^2 - \tilde{E}_{\mathbf{k}\lambda}^2 + P_{14}^2(\mathbf{k},\omega)]} \cdot \frac{[\omega^2 - c^2k^2 - \tilde{\omega}_p^2 - 4ck\omega_{\mathbf{k}\xi} P_{23}^2(\mathbf{k},\omega)/(\omega^2 - \tilde{\omega}_{\mathbf{k}\xi}^2)]}{[1 - \tilde{\Lambda}(\mathbf{k},\omega)][\omega^2 \tilde{\eta}^2(\mathbf{k},\omega) - c^2k^2]} \end{aligned} \tag{3.16a}$$

$$D_R(\mathbf{k},\omega) = \langle\langle \bar{A}_{\mathbf{k}\epsilon}; \bar{A}_{\mathbf{k}\epsilon}^{\dagger}\rangle\rangle = \left(\frac{1}{\pi}\right) \cdot \frac{ck}{[\omega^2 \tilde{\eta}^2(\mathbf{k},\omega) - c^2k^2]}, \tag{3.16b}$$

$$\begin{aligned} D_L(\mathbf{k},\omega) &= \langle\langle \bar{b}_{\mathbf{k}\xi}; \bar{b}_{\mathbf{k}\xi}^{\dagger}\rangle\rangle = \left(\frac{1}{\pi}\right) \cdot \left[\frac{\omega_{\mathbf{k}\xi}}{\omega^2 - \tilde{\omega}_{\mathbf{k}\xi}^2}\right] \\ &\times \frac{(\omega^2 - c^2k^2 - \tilde{\omega}_p^2 - 4ck) \sum |\tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2 [\tilde{E}_{\mathbf{k}\lambda} + P_{14}(\mathbf{k}\omega)]/[\omega^2 - \tilde{E}_{\mathbf{k}\lambda}^2 + P_{14}^2(\mathbf{k}\omega)]}{[1 - \tilde{\Lambda}(\mathbf{k},\omega)][\omega^2 \tilde{\eta}^2(\mathbf{k},\dot{\omega}) - c^2k^2]} \end{aligned} \tag{3.16c}$$

where the frequency and wave-vector dependent index of refraction is given by

$$\tilde{\eta}^2(\mathbf{k},\omega) = 1 - \left(\frac{\tilde{\omega}_p^2}{\omega^2}\right) - \sum_{\lambda\epsilon} \frac{4ck|\tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2[\tilde{E}_{\mathbf{k}\lambda} + P_{14}(\mathbf{k},\omega)]}{\omega^2[\omega^2 - \tilde{E}_{\mathbf{k}\lambda}^2 + P_{14}^2(\mathbf{k},\omega)][1 - \tilde{\Lambda}(\mathbf{k},\omega)]}$$

$$- \frac{4ck\omega_{\mathbf{k}\xi} P_{23}^2(\mathbf{k},\omega)}{\omega^2(\omega^2 - \tilde{\omega}_{\mathbf{k}\xi}^2)[1 - \tilde{\Lambda}(\mathbf{k},\omega)]} + \sum_{\substack{\lambda'\epsilon'\\ \xi'}} \frac{8ck\omega_{\mathbf{k}\xi}[\tilde{E}_{\mathbf{k}\lambda} + P_{14}(\mathbf{k},\omega)]}{\omega^2(\omega^2 - \tilde{\omega}_{\mathbf{k}\xi}^2)[\omega^2 - \tilde{E}_{\mathbf{k}\lambda}^2 + P_{14}^2(\mathbf{k},\omega)]}$$

$$\times \left[\frac{\tilde{f}_{\mathbf{k}\epsilon'}(\mathbf{k}\lambda)\,\tilde{g}^*_{-\mathbf{k}\xi}(\mathbf{k}\lambda')\,P_{23}(\mathbf{k},\omega) + \tilde{g}_{\mathbf{k}\xi'}(\mathbf{k}\lambda)\,\tilde{f}^*_{-\mathbf{k}\epsilon}(\mathbf{k}\lambda')\,P^*_{23}(\mathbf{k},\omega)}{1 - \tilde{\Lambda}(\mathbf{k},\omega)}\right], \tag{3.17a}$$

and the lattice response function, representing the polar field correction, is

$$1 - \tilde{\Lambda}(\mathbf{k},\omega) = 1 - \sum_{\lambda\xi} \frac{4\omega_{\mathbf{k}\xi}|\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2[\tilde{E}_{\mathbf{k}\lambda} + P_{14}(\mathbf{k},\omega)]}{(\omega^2 - \tilde{\omega}_{\mathbf{k}\xi}^2)[\omega^2 - \tilde{E}_{\mathbf{k}\lambda}^2 + P_{14}^2(\mathbf{k}\omega)]}. \tag{3.17b}$$

Use has been made of the following definitions

$$\tilde{E}_{\mathbf{k}\lambda} = \bar{E}_{\mathbf{k}\lambda} + \frac{1}{2\pi}\langle\langle S_{\mathrm{ex}}(\mathbf{k})\,;\,S_{\mathrm{ex}}^\dagger(\mathbf{k})\rangle\rangle = \bar{E}_{\mathbf{k}\lambda} + P_{11}(\mathbf{k},\omega), \tag{3.18a}$$

$$\tilde{\omega}_{\mathbf{k}\xi}^2 = \bar{\omega}_{\mathbf{k}\xi}^2 + \frac{\omega_{\mathbf{k}\xi}}{\pi}\langle\langle S_L(\mathbf{k})\,;\,S_L^\dagger(\mathbf{k})\rangle\rangle = \bar{\omega}_{\mathbf{k}\xi}^2 + P_{33}(\mathbf{k},\omega), \tag{3.18b}$$

$$\tilde{\omega}_p^2 = \omega_p^2 + \frac{ck}{\pi}\langle\langle S_R(\mathbf{k})\,;S_R^\dagger(\mathbf{k})\rangle\rangle = \omega_p^2 + P_{22}(\mathbf{k},\omega), \tag{3.18c}$$

$$P_{14}(\mathbf{k},\omega) = P_{41}^*(\mathbf{k},\omega) = \frac{1}{2\pi}\langle\langle S_{\mathrm{ex}}(\mathbf{k})\,;\,S_{\mathrm{ex}}(-\mathbf{k})\rangle\rangle, \tag{3.18d}$$

$$P_{23}(\mathbf{k},\omega) = P_{32}^*(\mathbf{k},\omega) = \frac{1}{2\pi}\langle\langle S_L(\mathbf{k})\,;S_R^\dagger(\mathbf{k})\rangle\rangle \tag{3.18e}$$

$$\sum_\xi \tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda) = \sum_\xi g_{\mathbf{k}\xi}(\mathbf{k}\lambda) + \frac{1}{2\pi}\langle\langle S_{\mathrm{ex}}(\mathbf{k})\,;S_L^\dagger(\mathbf{k})\rangle\rangle, \tag{3.18f}$$

$$\sum_\epsilon \tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda) = \sum_\epsilon \bar{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda) + \frac{1}{2\pi}\langle\langle S_{\mathrm{ex}}(\mathbf{k})\,;S_R^\dagger(\mathbf{k})\rangle\rangle, \tag{3.18g}$$

as well as for renormalized quantities

$$\bar{E}_{\mathbf{k}\lambda} = E_{\mathbf{k}\lambda} + \langle[S_{\mathrm{ex}}(\mathbf{k}),\alpha_{\mathbf{k}\lambda}^\dagger]_-\rangle_{t=t'} = E_{\mathbf{k}\lambda} + \sum_{\mathbf{k}'\xi'} D_{\mathbf{k}'\xi'-\mathbf{k}'\xi'}(\mathbf{k}\lambda,\mathbf{k}\lambda)\langle\bar{b}_{\mathbf{k}'\xi'}\bar{b}_{\mathbf{k}'\xi'}^\dagger\rangle, \tag{3.19a}$$

$$\bar{\omega}_{\mathbf{k}\xi}^2 = \omega_{\mathbf{k}\xi}^2 + \left\langle\left[S_L(\mathbf{k}),\frac{\omega\bar{b}_{\mathbf{k}\xi}^\dagger + \omega_{\mathbf{k}\xi}\tilde{b}_{\mathbf{k}\xi}^\dagger}{2\omega_{\mathbf{k}\xi}}\right]_-\right\rangle_{t=t'} = \omega_{\mathbf{k}\xi}^2 + \sum_{\mathbf{k}'\lambda'} 4\omega_{\mathbf{k}\xi}$$

$$\times D_{\mathbf{k}\xi,-\mathbf{k}\xi}(\mathbf{k}'\lambda',\mathbf{k}'\lambda')\langle\alpha_{\mathbf{k}'\lambda'}^\dagger\alpha_{\mathbf{k}'\lambda'}\rangle, \tag{3.19b}$$

$$\sum_{\epsilon} \bar{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda) = \sum_{\epsilon} f_{\mathbf{k}\epsilon}(\mathbf{k}\lambda) + \sum_{\mathbf{k}'\xi'} \theta_{\mathbf{k}'\xi'-\mathbf{k}'\xi'}(\mathbf{k}\lambda, \mathbf{k}\epsilon)\langle \bar{b}_{\mathbf{k}'\xi'} \bar{b}^{\dagger}_{\mathbf{k}'\xi'} \rangle. \tag{3.19c}$$

The renormalized quantities (3.19) are corrected by the static component of the scattering operator and are temperature dependent through the exciton and phonon occupation numbers, whereas the quantities (3.18) contain both the static and dynamic parts of the scattering operator. The latter contribution is made of a linear combination of many-particle Green functions and is a complex quantity.

The square of the index of refraction, $\tilde{\eta}^2(\mathbf{k}, \omega)$, is a function of the frequency ω and wave-vector $\mathbf{k}$ and depends on temperature through the renormalized quantities (3.19). It describes physical processes of the polariton-type excitations, arising from the exciton-lattice and exciton-radiation interactions in a dielectric medium. The first two terms in (3.17a) represent the usual high frequency index of refraction

$$\eta_{\infty}^2 = 1 - \frac{\tilde{\omega}_p^2}{\omega^2},$$

where $\tilde{\omega}_p^2$ is the square of the plasma frequency corrected by the component $P_{22}(\mathbf{k}, \omega)$ of the scattering operator, which takes into account direct photon scattering arising from the anharmonic interactions contained in $H^2 + H^3$. The third term in (3.17a) represents coupled excitations of the polariton type in the optical region of the spectrum, including anharmonic interactions through the scattering components $P_{11}(\mathbf{k}, \omega)$ and $P_{14}(\mathbf{k}, \omega)$. Its importance depends mostly on the exciton-photon coupling constant $\bar{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)$, given by (3.18g) and the anharmonic correction $\langle\langle S_{\mathrm{ex}}(\mathbf{k}); S_R^{\dagger}(\mathbf{k})\rangle\rangle$ will be neglected from now on, being of second order. The temperature dependence of the term in question arises through the renormalization parts of the oscillator strength $|\bar{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2$ and of the excitonic energy $\tilde{E}_{\mathbf{k}\lambda}$; the magnitude of the thermal effects depends on the strength of the quartic anharmonic coupling functions appearing in H^3_{eeLL} and H^3_{eRLL}. The usual expression for the polarizability in (3.17a) is modified by the lattice response function $1 - \tilde{\Lambda}(\mathbf{k}, \omega)$, the importance of which is given by the magnitude of the exciton-lattice coupling function $\tilde{g}_{\mathbf{k}\lambda}(\mathbf{k}\lambda)$; this modification can be substantial in polar crystals, where the Fröhlich interaction is usually important. It results in an indirect lattice-radiation coupling via exciton states.

The fourth term in (3.17a) is a lattice contribution representing polariton-like excitations, in which the second-order oscillator strength $|P_{23}(\mathbf{k}, \omega)|^2$ arises from anharmonic interactions between the radiation and the lattice; it contributes to $\tilde{\eta}^2(\mathbf{k}, \omega)$ only in the infrared region and it will be discarded from now on. The last contribution in (3.17a) is a higher order correction, which will be also neglected; it represents anharmonic couplings between the exciton, phonon and photon fields and it can be split into two corrections to the third and fourth terms of $\tilde{\eta}^2(\mathbf{k}, \omega)$.

The Green functions (3.16) describe the behaviour of the coupled system, which consists of the exciton, photon and phonon fields. These fields are coupled through the H^1 interactions and the Green functions have, therefore, the same poles or singularities located at the energies $\omega_\rho(\mathbf{k})$, which are solutions of the secular equation

$$\omega^2 \operatorname{Re} \tilde{\eta}^2(\mathbf{k}, \omega) - c^2 k^2 = 0. \tag{3.20}$$

For a given wavevector $\mathbf{k}$, these roots $\omega_\rho(\mathbf{k})$ give the renormalized polariton energies of excitation with branch index ρ. The excitation spectrum will be examined in the following section in successive approximations. But, before that, we will consider three limiting cases, which will be needed later.

Limiting cases

a) In the range of wave-vectors where dispersion can be ignored, we can let $|f_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2$ vanish and then from (3.16), we have

$$D^b_{\mathrm{ex}}(\mathbf{k},\omega) = \left(\frac{1}{\pi}\right)\left[\frac{\tilde{E}_{\mathbf{k}\lambda} + P_{14}(\mathbf{k},\omega)}{\omega^2 - \tilde{E}^2_{\mathbf{k}\lambda} + P^2_{14}(\mathbf{k},\omega)}\right]\frac{1}{1-\tilde{\Lambda}(\mathbf{k},\omega)}, \tag{3.21a}$$

$$D^b_L(\mathbf{k},\omega) = \left(\frac{1}{\pi}\right)\left[\frac{\omega_{\mathbf{k}\xi}}{\omega^2 - \tilde{\omega}^2_{\mathbf{k}\xi}}\right]\frac{1}{1-\tilde{\Lambda}(\mathbf{k},\omega)}, \tag{3.21b}$$

$$D^b_R(\mathbf{k},\omega) = \left(\frac{1}{\pi}\right)\left[\frac{ck}{\omega^2 - c^2k^2 - \tilde{\omega}^2_p}\right]. \tag{3.21c}$$

In this case the exciton and the phonon fields are coupled, while the photon field is independent. $D^b_R(\mathbf{k},\omega)$ is the bare photon Green's function corrected for direct photon scattering effects through $\tilde{\omega}^2_p$. The excitation spectrum for the photon field is determined by the roots of the equation

$$\omega^2 - c^2k^2 - \omega^2_p - \mathrm{Re}\,P_{22}(\mathbf{k},\omega) = 0, \tag{3.22a}$$

while $\mathrm{Im}\,P_{22}(\mathbf{k},\omega)$ describes various photon decay mechanisms. The excitation spectrum of the coupled exciton-phonon fields is determined by the roots of the following equation, which is obtained by equating to zero the real part of the denominator of (3.21a) or (3.21b), i.e.,

$$(\omega^2 - \mathrm{Re}\,\tilde{\omega}^2_{\mathbf{k}\xi})[\omega^2 - \mathrm{Re}\,\tilde{E}^2_{\mathbf{k}\lambda} + \mathrm{Re}\,P_{14}(\mathbf{k},\omega)] - \mathrm{Im}\,\tilde{\omega}^2_{\mathbf{k}\xi}[\mathrm{Im}\,\tilde{E}^2_{\mathbf{k}\lambda} - \mathrm{Im}\,P^2_{14}(\mathbf{k},\omega)]$$
$$- \sum_{\lambda\xi} 4\omega_{\mathbf{k}\xi}|\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2\,\mathrm{Re}[\tilde{E}_{\mathbf{k}\lambda} + P_{14}(\mathbf{k},\omega)] = 0, \tag{3.22b}$$

whereas its imaginary part, $\Gamma^b(\mathbf{k},\omega)$, given by

$$-(\omega^2 - \mathrm{Re}\,\tilde{\omega}^2_{\mathbf{k}\xi})[\mathrm{Im}\,\tilde{E}^2_{\mathbf{k}\lambda} - \mathrm{Im}\,P^2_{14}(\mathbf{k},\omega)] - \mathrm{Im}\,\tilde{\omega}^2_{\mathbf{k}\xi}[\omega^2 - \mathrm{Re}\,\tilde{E}^2_{\mathbf{k}\lambda} + \mathrm{Re}\,P^2_{14}(\mathbf{k},\omega)]$$
$$- \sum_{\lambda\xi} 4\omega_{\mathbf{k}\xi}|\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2\,\mathrm{Im}[\tilde{E}_{\mathbf{k}\lambda} + P_{14}(\mathbf{k},\omega)] = \Gamma^b(\mathbf{k},\omega) \tag{3.22c}$$

represents the lifetime broadening arising from the various scattering events leading to the decay of the incoming particle. The results obtained in this case are similar to those achieved in the lowest order when the exciton-photon interaction H^1_{eR} is treated within the framework of perturbation theory.

b) The specific case, where the exciton and the photon fields are coupled, while the phonon field is independent, occurs when the exciton-lattice interaction is vanishingly small. Taking the limit $|g_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2 = 0$ in (3.16) leads to

$$D^u_{\mathrm{ex}}(\mathbf{k},\omega) = \left(\frac{1}{\pi}\right)\left[\frac{\tilde{E}_{\mathbf{k}\lambda} + P_{14}(\mathbf{k},\omega)}{\omega^2 - \tilde{E}^2_{\mathbf{k}\lambda} + P^2_{14}(\mathbf{k},\omega)}\right]\frac{[\omega^2 - c^2k^2 - \tilde{\omega}^2_p]}{[\omega^2\tilde{\eta}^2_u(\mathbf{k},\omega) - c^2k^2]}, \tag{3.23a}$$

$$D^u_R(\mathbf{k},\omega) = \left(\frac{1}{\pi}\right)\left[\frac{ck}{[\omega^2\tilde{\eta}^2_u(\mathbf{k},\omega) - c^2k^2]}\right], \tag{3.23b}$$

$$D_L^u(\mathbf{k},\omega) = \left(\frac{1}{\pi}\right)\left[\frac{\omega_{\mathbf{k}\xi}}{\omega^2 - \tilde{\omega}^2_{\mathbf{k}\xi}}\right], \tag{3.23c}$$

$$\tilde{\eta}_u^2(\mathbf{k},\omega) = 1 - \frac{\tilde{\omega}_p^2}{\omega^2} - \frac{1}{\omega^2}\sum_{\lambda\epsilon}\frac{4ck|\tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2[\tilde{E}_{\mathbf{k}\lambda} + P_{14}(\mathbf{k},\omega)]}{[\omega^2 - \tilde{E}^2_{\mathbf{k}\lambda} + P^2_{14}(\mathbf{k},\omega)]}. \tag{3.23d}$$

The excitation spectrum of the mechanical phonon field is given by the roots of the equation

$$\omega^2 - \operatorname{Re}\tilde{\omega}^2_{\mathbf{k}\xi} = 0, \tag{3.24a}$$

while the energies of excitation corresponding to the bare polariton spectrum are determined by the solutions of the equation

$$\omega^2 \operatorname{Re}\tilde{\eta}_u^2(\mathbf{k},\omega) - c^2k^2 = 0. \tag{3.24b}$$

Both spectra include corrections arising from anharmonic interactions. The Green functions (3.23) give the same results when the bare polariton-photon interaction is treated by means of perturbation theory, as it has been done by Bendow and Birman [12].

c) Finally in the case when the three fields are independent of one another, then from (3.16) we have

$$D_{\mathrm{ex}}^F(\mathbf{k},\omega) = \left(\frac{1}{\pi}\right)\left[\frac{\tilde{E}_{\mathbf{k}\lambda} + P_{14}(\mathbf{k},\omega)}{\omega^2 - \tilde{E}^2_{\mathbf{k}\lambda} + P^2_{14}(\mathbf{k},\omega)}\right], \tag{3.25a}$$

$$D_R^F(\mathbf{k},\omega) = \left(\frac{1}{\pi}\right)\left[\frac{ck}{\omega^2 - c^2k^2 - \tilde{\omega}_p^2}\right], \tag{3.25b}$$

$$D_L^F(\mathbf{k},\omega) = \left(\frac{1}{\pi}\right)\left[\frac{\omega_{\mathbf{k}\xi}}{\omega^2 - \tilde{\omega}^2_{\mathbf{k}\xi}}\right]. \tag{3.25c}$$

The Green functions $D_{\mathrm{ex}}^F(\mathbf{k},\omega)$, $D_R^F(\mathbf{k},\omega)$ and $D_L^F(\mathbf{k},\omega)$ describe physical processes, where free excitons, free photons and free phonons are scattered independently by their own anharmonic fields respectively. The excitation spectrum of each field is described by the poles of the corresponding Green function.

IV. Excitation Spectrum

We shall discuss the excitation spectrum for the three coupled fields described by the Green functions (3.15) or (3.16). In this section, only the static approximation will be considered, while dynamic effects will be discussed in the next section. In the static approximation, the Green function $D(\mathbf{k},\omega)$ is given by the first two terms in the expression (3.15). Since two terms are involved in the expression (3.15), the excitation spectrum will be considered in two successive approximations.

a) Zero-order approximation

In the zero-order approximation, all anharmonic interactions are ignored and the scattering operator is, therefore, set equal to zero; i.e., only the first term in (3.15) is retained and it will be denoted by the subscript (00). Then, from (3.16) or (3.7) and (3.8), the Green functions can be written as

$$D_{\mathrm{ex}(00)}(\mathbf{k},\omega) = \frac{1}{\pi}\left(\frac{E_{\mathbf{k}\lambda}}{\omega^2 - E_{\mathbf{k}\lambda}^2}\right)\cdot\frac{(\omega^2 - c^2k^2 - \omega_p^2)}{[\omega^2\eta_{(00)}^2(\mathbf{k},\omega) - c^2k^2]}\,\frac{1}{[1 - \Lambda_{(00)}(\mathbf{k},\omega)]}, \tag{4.1a}$$

$$D_{R(00)}(\mathbf{k},\omega) = \frac{1}{\pi}\,\frac{ck}{[\omega^2\eta_{(00)}^2(\mathbf{k},\omega) - c^2k^2]}, \tag{4.1b}$$

$$D_{L(00)}(\mathbf{k},\omega) = \frac{1}{\pi}\left(\frac{\omega_{\mathbf{k}\xi}}{\omega^2 - \omega_{\mathbf{k}\xi}^2}\right)\frac{\omega^2 - c^2k^2 - \omega_p^2 - 4ck\sum_{\lambda\epsilon}|f_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2E_{\mathbf{k}\lambda}/(\omega^2 - E_{\mathbf{k}\lambda}^2)}{[\omega^2\eta_{(00)}^2(\mathbf{k},\omega) - c^2k^2][1 - \Lambda_{(00)}(\mathbf{k},\omega)]}, \tag{4.1c}$$

where the square of the index of refraction and the lattice response function are given by:

$$\eta_{(00)}^2(\mathbf{k},\omega) = \eta_\infty^2 - 4ck\sum_{\lambda\epsilon}\frac{E_{\mathbf{k}\lambda}|f_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2}{\omega^2(\omega^2 - E_{\mathbf{k}\lambda}^2)}\cdot\frac{1}{[1 - \Lambda_{(00)}(\mathbf{k},\omega)]} \tag{4.2a}$$

$$\eta_\infty^2 = 1 - \frac{\omega_p^2}{\omega^2}, \tag{4.2b}$$

$$1 - \Lambda_{(00)}(\mathbf{k},\omega) = 1 - 4\sum_{(\lambda)\xi}\frac{\omega_{\mathbf{k}\xi}E_{\mathbf{k}\lambda}|g_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2}{(\omega^2 - E_{\mathbf{k}\lambda}^2)(\omega^2 - \omega_{\mathbf{k}\xi}^2)}. \tag{4.2c}$$

In (4.2a), the ϵ-summation runs over the two transverse polarizations of the photon and the λ-summation is extended over all the indexes and quantum numbers which characterize the exciton. The latter is also applied to the exciton index λ, which appears in the lattice response function, where the ξ-sum runs over all the phonon branches; this restriction to the λ-sum in the lattice response function is denoted by the parentheses affecting the exciton index (λ) in (4.2c).

The square of the index of refraction $\eta_{(00)}^2(\mathbf{k},\omega)$ is a well-behaved function of the wave-vector and the frequency. Its first term η_∞^2, given in (4.2b), is the usual high frequency dielectric function, which is obtained when the limit of large ω is taken. Its second term represents coupled excitations of the dressed polariton type, the dressing being represented by the lattice response function defined in (4.2c). It can be rewritten in terms of the usual excitonic polarizability $\alpha_{(00)}(\mathbf{k},\omega)$ which represents the dispersion effects contained in H_{eR}^1.

$$\alpha_{(00)}(\mathbf{k},\omega) = \sum_{\lambda\epsilon}\frac{E_{\mathbf{k}\lambda}|f_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2}{E_{\mathbf{k}\lambda}^2 - \omega^2}, \tag{4.3a}$$

$$\eta_{(00)}^2(\mathbf{k},\omega) = \eta_\infty^2 + \frac{4ck}{\omega^2}\cdot\frac{\alpha_{(00)}(\mathbf{k},\omega)}{1 - \Lambda_{(00)}(\mathbf{k},\omega)}. \tag{4.3b}$$

It can be seen that the exciton-phonon interaction H_{eL}^1 results in a modification of the usual polarizability contribution by the lattice response function—or lattice polarizability—which represents the polar field correction. Its importance depends on the magnitude of the exciton-phonon coupling constant $g_{\mathbf{k}\xi}(\mathbf{k}\lambda)$, which can be large in polar crystals, where the Fröhlich mechanism exists. This interaction induces an indirect photon-phonon coupling via exciton states, which shifts the dispersion frequency $E_{\mathbf{k}\lambda}$ of the polarizability term to higher energies and introduces a new dispersion frequency in the neighbourhood of phonon energies. If the present model is applied to the case of CdS, as has been done by other authors [3], [4], [12], we find, using the data of Rode [13], that the coupling via Fröhlich interaction alone between the 1s exciton of the A series and the LO phonon shifts the zeros of the denominator in (4.2a) by 7 meV towards higher energy.

The expression (4.2a) for the index of refraction can be compared with the expression of Bendow et al. [12], [14]. If we consider, as they did, that the mechanical oscillators—excitons and phonons—are weakly interacting, then we can take in the lattice response function the limit of small $|g_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2$ and expand $[1 - \Lambda_{(00)}(\mathbf{k}, \omega)]^{-1}$ in power series of $\Lambda_{(00)}(\mathbf{k}, \omega)$. Then, retaining only the first term, we recover Bendow's expression for the dielectric function.

The behaviour of the system of dressed polaritons in the absence of any anharmonic interaction is described by the functions (4.1). Their common poles, located at the energies $\omega_{\rho(00)}(\mathbf{k})$, are solutions of the secular equation

$$\omega^2 \eta^2_{(00)}(\mathbf{k}, \omega) - c^2 k^2 = 0. \tag{4.4}$$

The energies of excitation $\omega_{\rho(00)}(\mathbf{k})$ describe the dressed (by the phonon field) polariton modes with band index ρ and wave-vector $\mathbf{k}$. The number of branches is, of course, equal to the total number of modes and, hence, no analytical expression for $\omega_{\rho(00)}(\mathbf{k})$ as a function of the wave-vector will be given. The excitation spectrum has to be computed numerically for actual crystals with appropriate values for the bare modes energy and coupling functions. If we consider the simple case of a crystal with a single exciton level coupled to a single phonon branch, it can be said that, for a wave-vector such that ck is in the excitonic region, the two branches in the high energy part of the spectrum are mostly polaritons with a small phonon content, while the low energy branch is mostly phonon with a small polariton contribution. The degree of mixing depends, of course, on the strength of both first-order coupling functions.

The dressed polariton excitation spectrum is also obtained through a complete diagonalization of the first-order Hamiltonian $H^0 + H^1$, which can be written as

$$\mathscr{H}^{\text{pol}}_{(00)} = E_{(00)} + \sum_{\mathbf{k}\rho} \omega_{\rho(00)}(\mathbf{k})\, \gamma^{\dagger}_{\rho(00)}(\mathbf{k})\, \gamma_{\rho(00)}(\mathbf{k}). \tag{4.5}$$

In this expression, $E_{(00)}$ is the average energy of the dressed polariton field, $\omega_{\rho(00)}(\mathbf{k})$ is the energy of excitation of the ($\rho\mathbf{k}$) dressed polariton and $\gamma^{\dagger}_{\rho(00)}(\mathbf{k})$, $\gamma_{\rho(00)}(\mathbf{k})$ are the dressed polariton ($\rho\mathbf{k}$) creation and annihilation operators, in the zero-order approximation respectively. These dressed polariton operators are made of the admixture of exciton, photon and phonon operators given by

$$\begin{aligned}
\alpha_{\mathbf{k}\lambda} &= \sum_{\rho} [u^{(00)}_{\lambda\rho}(\mathbf{k})\, \gamma_{\rho(00)}(\mathbf{k}) + v^{(00)}_{\lambda\rho}(\mathbf{k})\, \gamma^{\dagger}_{\rho(00)}(-\mathbf{k})],\\
b_{\mathbf{k}\xi} &= \sum_{\rho} [u^{(00)}_{\xi\rho}(\mathbf{k})\, \gamma_{\rho(00)}(\mathbf{k}) + v^{(00)}_{\xi\rho}(\mathbf{k})\, \gamma^{\dagger}_{\rho(00)}(-\mathbf{k})],\\
A_{\mathbf{k}\epsilon} &= \sum_{\rho} [u^{(00)}_{\epsilon\rho}(\mathbf{k})\, \gamma_{\rho(00)}(\mathbf{k}) + v^{(00)}_{\epsilon\rho}(\mathbf{k})\, \gamma^{\dagger}_{\rho(00)}(-\mathbf{k})],
\end{aligned} \tag{4.6}$$

together with the complex conjugate relations for the creation operators. The amplitude $u_{jp}^{(00)}(\mathbf{k})$ and $v_{jp}^{(00)}(\mathbf{k}), j=\lambda, \xi, \epsilon$, of the Bogoliubov's canonical transformation (4.6), which brings the Hamiltonian H^0+H^1 into the diagonal form (4.5), can be obtained by performing the canonical transformation and using the appropriate commutation relations. It is a rather lengthy and tedious procedure and they are more easily obtained using that fact [15] that the u's and v's are equal to the distribution functions taken in the limit of zero temperature. Bendow's [14] coefficients ϕ and χ can be recovered from ours if the first-order exciton lattice coupling is ignored by setting $|g_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2=0$ and taking $\omega_p^2=0$. This leads to the limiting case b) of the preceding section, where polaritons interact anharmonically with bare phonons.

It is known that the dielectric function is proportional to the exciton Green function [11], [6] so that the absorption line shape is given by the exciton spectral function $J_{\mathrm{ex}(00)}(\mathbf{k},\omega)$. Since all quantities in (4.1) and (4.2) are real, the exciton Green function is real. Hence, the spectral function and, therefore, the absorption coefficient consists of δ-shaped lines, peaked at the poles $\omega_{\rho(00)}(\mathbf{k})$

$$\begin{aligned} J_{\mathrm{ex}(00)}(\mathbf{k},\omega) &= (e^{\beta\omega}-1)^{-1}\, i \lim_{\epsilon\to 0}[D_{\mathrm{ex}(00)}(\mathbf{k},\omega-i\epsilon)-D_{\mathrm{ex}(00)}(\mathbf{k},\omega+i\epsilon)] \\ &= \sum_{\rho}(e^{\beta\omega}-1)^{-1}\left(\frac{2E_{\mathbf{k}\lambda}}{\omega^2-E_{\mathbf{k}\lambda}^2}\right)\cdot\frac{(\omega^2-c^2k^2-\omega_p^2)}{[1-\Lambda_{(00)}(\mathbf{k},\omega)]}\cdot\frac{\lambda_{(00)}(\mathbf{k}\rho)}{\omega_{\rho(00)}(\mathbf{k})}[\delta(\omega-\omega_{\rho(00)}(\mathbf{k})) \\ &\quad -\delta(\omega+\omega_{\rho(00)}(\mathbf{k}))], \end{aligned} \tag{4.7}$$

where $\beta=(k_B T)^{-1}$ with k_B being the Boltzmann constant and T the absolute temperature. We have used the screening factor $\lambda_{(00)}(\mathbf{k}\rho)$ defined as

$$\lambda_{(00)}(\mathbf{k}\rho)=\left(\frac{d\omega^2\,\eta_{(00)}^2(\mathbf{k},\omega)}{d\omega^2}\right)^{-1}_{\omega=\omega_{\rho(00)}(\mathbf{k})}. \tag{4.8}$$

This factor represents the effect of the polarization of the medium and is closely related to the energy transport velocity [4], [16]. Far from the dispersion region or if the dispersion is weak, the screening factor reduces to

$$\lambda_{(00)}(\mathbf{k}\rho)=\eta_{(00)}^{-2}(\mathbf{k},\omega_{\rho(00)}).$$

As has been said earlier, the distribution function obtained from (4.7) obeys the relation [11]

$$\lim_{T=0}\langle\tilde{\alpha}_{\mathbf{k}\lambda}\tilde{\alpha}_{\mathbf{k}\lambda}^{\dagger}\rangle_{(00)}=\lim_{T=0}\int_{-\infty}^{+\infty}J_{\mathrm{ex}(00)}(\mathbf{k},\omega)\,d\omega=\sum_{\rho}|u_{\lambda\rho}^{(00)}(\mathbf{k})-v_{\lambda\rho}^{(00)}(\mathbf{k})|^2.$$

b) Zero-order renormalized approximation

In this approximation, we take into account the static part of the scattering operator $\langle[S(\mathbf{k}),B_{\mathbf{k}}^{\dagger}]_-\rangle_{t=t'}$, the second term in (3.15), while the dynamic component is ignored. To calculate the matrix elements of this correction, we will assume that all the average values of single operators as well as those of products of operators corresponding to particles of different kind represent second-order contributions, which can be neglected. The remaining contributions are given by the last terms in (3.19) arising from quartic anharmonicity.

The thermal distribution functions, which appear in the last terms of (3.19) are calculated in the zero-order approximation, using the Green functions (4.1). They are given by

$$\langle \alpha^{\dagger}_{\mathbf{k}\lambda}\alpha_{\mathbf{k}\lambda}\rangle = N^{(00)}_{\lambda}(\mathbf{k}) = \sum_{\rho} \frac{\lambda_{(00)}(\mathbf{k}\rho)}{\omega_{\rho(00)}(\mathbf{k})} \cdot \frac{ck\alpha_{(00)}(\mathbf{k}\rho)}{[1-\Lambda_{(00)}(\mathbf{k}\rho)]^2}\left[\frac{E_{\mathbf{k}\lambda}-\omega_{\rho(00)}(\mathbf{k})}{E_{\mathbf{k}\lambda}+\omega_{\rho(00)}(\mathbf{k})}\right]$$

$$\cdot \frac{1}{E_{\mathbf{k}\lambda}} \coth\frac{\beta\omega_{\rho(00)}}{2} = \sum_{\rho} |v^{(00)}_{\lambda\rho}(\mathbf{k})|^2 \coth\frac{\beta\omega_{\rho(00)}}{2}, \tag{4.9a}$$

$$\langle \bar{b}_{\mathbf{k}\xi}\bar{b}_{\mathbf{k}\xi}\rangle_{(00)} = \bar{N}^{(00)}_{\xi}(\mathbf{k}) = \sum_{\rho} \frac{\lambda_{(00)}(\mathbf{k}\rho)}{\omega_{\rho(00)}(\mathbf{k})} \cdot \frac{4ck\alpha_{(00)}(\mathbf{k}\rho)\,\Lambda_{(00)}(\mathbf{k}\rho)}{[1-\Lambda_{(00)}(\mathbf{k}\rho)]^2}$$

$$\cdot \frac{\omega_{\mathbf{k}\xi}}{[\omega^2_{\mathbf{k}\xi}-\omega^2_{\rho(00)}(\mathbf{k})]} \coth\frac{\beta\omega_{\rho(00)}}{2} = \sum_{\rho} |u^{(00)}_{\xi\rho}(\mathbf{k}) + v^{(00)}_{\xi\rho}(\mathbf{k})|^2 \coth\frac{\beta\omega_{\rho(00)}}{2}. \tag{4.9b}$$

For a vanishing first-order interaction H^1, (4.9a) and (4.9b) are reduced to the well-known distribution functions for the free exciton and phonon fields respectively, i.e.,

$$\langle \alpha^{\dagger}_{\mathbf{k}\lambda}\alpha_{\mathbf{k}\lambda}\rangle_{(00)} = 0$$

$$\langle \bar{b}_{\mathbf{k}\xi}\bar{b}^{\dagger}_{\mathbf{k}\xi}\rangle_{(00)} = \coth\frac{\beta\omega_{\mathbf{k}\xi}}{2} = 1 + 2N^{(00)}_{\xi}(\mathbf{k}). \tag{4.10}$$

Since the exciton energy is much larger than the thermal energy, the exciton distribution function is very small and can be neglected. Hence, the only non-negligible contributions are those proportional to the phonon occupation numbers. The excitonic energy is corrected through the second term in (3.19a), which amounts to

$$\Delta E_{\mathbf{k}\lambda}(T) = \sum_{\mathbf{k}'\xi'} D_{\mathbf{k}'\xi'-\mathbf{k}'\xi'}(\mathbf{k}\lambda,\mathbf{k}\lambda)\,\bar{N}^{(00)}_{\xi'}(\mathbf{k}'), \tag{4.11a}$$

and represents the energy shift arising from the scattering of the $(\mathbf{k}\lambda)$ exciton into itself with simultaneous emission and absorption of $(\mathbf{k}'\xi')$ phonon. The exciton-photon coupling parameter $f_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)$ is renormalized by

$$\Delta f_{\mathbf{k}\epsilon}(\mathbf{k}\lambda, T) = \sum_{\mathbf{k}'\xi'} \theta_{\mathbf{k}'\xi'-\mathbf{k}'\xi'}(\mathbf{k}\lambda,\mathbf{k}\epsilon)\,\bar{N}^{(00)}_{\xi'}(\mathbf{k}'), \tag{4.11b}$$

the interpretation of which is similar to that of $\Delta E_{\mathbf{k}\lambda}(T)$.

Both quantities in (4.11) are functions of temperature through the phonon distribution function. At high temperature, they are linearly increasing functions of T, and independent of temperature for $k_B T \ll \omega_{\rho(00)}(\mathbf{k})$. Both contributions arise from quartic anharmonic interactions among the dressed polaritons and, therefore, do not vanish in the absence of first-order coupling H^1.

Upon replacing the exciton energy and the oscillator strength by their renormalized values $\bar{E}_{\mathbf{k}\lambda}$ and $|\bar{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2$ in (4.1) and (4.2), we obtain the zero order renormalized Green functions and the corresponding secular equation. From the latter, we can derive the renormalized excitation spectrum $\omega_{\rho(0)}(\mathbf{k})$, which is temperature dependent and slightly shifted with respect to $\omega_{\rho(00)}(\mathbf{k})$. Since both renormalizing terms (4.11) are real, the new

Green functions are still real and the renormalized spectrum is also made of δ-shaped line peaked at the energies $\omega_{\rho(0)}(\mathbf{k})$. The significance of the temperature dependence of the excitation spectrum and the magnitude of the energy shift $\omega_{\rho(0)}(\mathbf{k}) - \omega_{\rho(00)}(\mathbf{k})$ depend on the importance of the renormalization terms, hence on the strength of the anharmonic interactions H^3_{eeLL} and H^3_{eRLL}. In (4.11), the summation is extended to all phonon branches ξ' and wave-vectors $\mathbf{k}'$. It is possible that, in polar crystals, where the Fröhlich interaction exists, renormalization may be of some importance. Thus, the inclusion of the static part of the polarization operator results only in a temperature dependent shift of the excitation spectrum.

V. Line Shape of Absorption Bands

To study the dynamic effects, which govern the shape of the absorption bands, we have to use the complete expression for the Green function (3.15) or its components given by (3.16)–(3.19). The dynamic part of the polarization operator is described by the function $P(\mathbf{k},\omega) = \langle\langle S(\mathbf{k}); S^{\dagger}(\mathbf{k})\rangle\rangle$, which is, in general, a complex quantity and represents various scattering processes caused by the anharmonic parts of the Hamiltonian $H^2 + H^3$. Taking the imaginary parts of the expressions for the Green functions (3.16), we find

$$- \operatorname{Im} D^{(1)}_{\text{ex}}(\mathbf{k},\omega) = \left(\frac{1}{\pi}\right)\left(\frac{\theta(\mathbf{k},\omega)}{\omega^2 - \hat{E}^2_{\mathbf{k}\lambda}}\right) \frac{\hat{\Gamma}(\mathbf{k},\omega) - [\omega^2 \operatorname{Re}\tilde{\eta}^2(\mathbf{k},\omega) - c^2 k^2]\,\hat{\mu}(\mathbf{k},\omega)/\theta(\mathbf{k},\omega)}{[\omega^2 \operatorname{Re}\tilde{\eta}^2(\mathbf{k},\omega) - c^2 k^2]^2 + [\hat{\Gamma}(\mathbf{k},\omega)]^2}, \tag{5.1a}$$

$$- \operatorname{Im} D^{(1)}_{R}(\mathbf{k},\omega) = \left(\frac{ck}{1}\right) \frac{\hat{\Gamma}(\mathbf{k},\omega) - [\omega^2 \operatorname{Re}\tilde{\eta}^2(\mathbf{k},\omega) - c^2 k^2]\,\hat{\gamma}(\mathbf{k},\omega)}{[\omega^2 \operatorname{Re}\tilde{\eta}^2(\mathbf{k},\omega) - c^2 k^2]^2 + [\hat{\Gamma}(\mathbf{k},\omega)]^2}, \tag{5.1b}$$

$$- \operatorname{Im} D^{(1)}_{L}(\mathbf{k},\omega) = \left(\frac{\omega_{\mathbf{k}\xi}}{\pi}\right)\left(\frac{\beta(\mathbf{k},\omega)}{\omega^2 - \hat{\omega}^2_{\mathbf{k}\xi}}\right) \frac{\hat{\Gamma}(\mathbf{k},\omega) - [\omega^2 \operatorname{Re}\hat{\eta}^2(\mathbf{k},\omega) - c^2 k^2]\,\hat{\delta}(\mathbf{k},\omega)/\beta(\mathbf{k},\omega)}{[\omega^2 \operatorname{Re}\tilde{\eta}^2(\mathbf{k},\omega) - c^2 k^2]^2 + [\hat{\Gamma}(\mathbf{k},\omega)]^2}. \tag{5.1c}$$

Use has been made of the following notation:

$$\hat{E}_{\mathbf{k}\lambda} = \bar{E}_{\mathbf{k}\lambda} + \operatorname{Re} P_{11}(\mathbf{k},\omega), \qquad \hat{E}^2_{\mathbf{k}\lambda} = \bar{E}^2_{\mathbf{k}\lambda} + 2\bar{E}_{\mathbf{k}\lambda} \operatorname{Re} P_{11}(\mathbf{k},\omega) \tag{5.2a}$$

$$\hat{\omega}^2_{\mathbf{k}\xi} = \omega^2_{\mathbf{k}\xi} + \operatorname{Re} P_{33}(\mathbf{k},\omega), \tag{5.2b}$$

$$\hat{\omega}^2_p = \omega^2_p + \operatorname{Re} P_{22}(\mathbf{k},\omega), \tag{5.2c}$$

$$\theta(\mathbf{k},\omega) = \frac{[\hat{E}_{\mathbf{k}\lambda} + \operatorname{Re} P_{14}(\mathbf{k},\omega)]}{[1 - \operatorname{Re}\tilde{\Lambda}(\mathbf{k},\omega)]}\,(\omega^2 - c^2 k^2 - \hat{\omega}^2), \tag{5.3a}$$

$$\hat{\mu}(\mathbf{k},\omega) = \frac{(\omega^2 - c^2 k^2 - \hat{\omega}^2_p)}{[1 - \operatorname{Re}\tilde{\Lambda}(\mathbf{k},\omega)]}\Bigg[\operatorname{Im}(P_{11} + P_{14}) - (\hat{E}_{\mathbf{k}\lambda} + \operatorname{Re} P_{14}) \times \left(\frac{\operatorname{Im} P_{33}}{(\omega^2 - \hat{\omega}^2_{\mathbf{k}\xi})} + \frac{\operatorname{Im} P_{22}}{(\omega^2 - c^2 k^2 - \hat{\omega}^2_p)}\right)\Bigg] \tag{5.3b}$$

$$\hat{\gamma}(\mathbf{k},\omega) = \frac{-1}{[1-\operatorname{Re}\tilde{\Lambda}(\mathbf{k},\omega)]}\cdot\left[\frac{2\bar{E}_{\mathbf{k}\lambda}\operatorname{Im}P_{11}}{(\omega^2-\hat{E}^2_{\mathbf{k}\lambda})}+\frac{\operatorname{Im}P_{33}}{(\omega^2-\hat{\omega}^2_{\mathbf{k}\xi})}\right.$$

$$\left.+\sum_{\lambda\xi}\frac{4\omega_{\mathbf{k}\xi}|\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2\operatorname{Im}(P_{11}+P_{14})}{(\omega^2-\hat{E}^2_{\mathbf{k}\lambda})\;(\omega^2-\hat{\omega}^2_{\mathbf{k}\xi})}\right], \tag{5.3c}$$

$$\beta(\mathbf{k},\omega) = \frac{1}{[1-\operatorname{Re}\tilde{\Lambda}(\mathbf{k},\omega)]}\left[\omega^2-c^2k^2-\hat{\omega}^2_p-\sum_{\lambda\epsilon}\frac{4ck|\tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2}{(\omega^2-\hat{E}^2_{\mathbf{k}\lambda})}(E_{\mathbf{k}\lambda}+\operatorname{Re}P_{14})\right], \tag{5.3d}$$

$$\hat{\delta}(\mathbf{k},\omega) = -\frac{(\omega^2-c^2k^2-\hat{\omega}^2_p)}{[1-\operatorname{Re}\tilde{\Lambda}(\mathbf{k},\omega)]}\left[\frac{2\bar{E}_{\mathbf{k}\lambda}\operatorname{Im}P_{11}}{(\omega^2-\hat{E}^2_{\mathbf{k}\lambda})}+\frac{\operatorname{Im}P_{22}}{(\omega^2-c^2k^2-\hat{\omega}^2_p)}\right.$$

$$\left.+\sum_{\lambda\epsilon}\frac{4ck|\tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2\operatorname{Im}(P_{11}+P_{14})}{(\omega^2-\hat{E}^2_{\mathbf{k}\lambda})(\omega^2-c^2k^2-\hat{\omega}^2_p)}\right]. \tag{5.3e}$$

The real parts of the square of the index of refraction and of the lattice response function are given by

$$\operatorname{Re}\tilde{\eta}^2(\mathbf{k},\omega) = \eta^2_\infty - \frac{\operatorname{Re}P_{22}}{\omega^2}-\frac{4ck}{\omega^2}\sum_{\lambda\epsilon}\frac{|\tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2(\hat{E}_{\mathbf{k}\lambda}+\operatorname{Re}P_{14})}{(\omega^2-\hat{E}^2_{\mathbf{k}\lambda})[1-\operatorname{Re}\Lambda(\mathbf{k},\omega)]}, \tag{5.4a}$$

$$1-\operatorname{Re}\tilde{\Lambda}(\mathbf{k},\omega) = 1-4\sum_{\lambda\xi}\frac{\omega_{\mathbf{k}\xi}|\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2(\hat{E}_{\mathbf{k}\lambda}+\operatorname{Re}P_{14})}{(\omega^2-\hat{E}^2_{\mathbf{k}\lambda})(\omega^2-\hat{\omega}^2_{\mathbf{k}\xi})}. \tag{5.4b}$$

The damping function, $\hat{\Gamma}(\mathbf{k},\omega)$, describes lifetime effects arising from the anharmonic interactions and has the form

$$\hat{\Gamma}(\mathbf{k},\omega) = -\operatorname{Im}P_{22}$$

$$-\frac{\operatorname{Im}P_{33}}{(\omega^2-\hat{\omega}^2_{\mathbf{k}\xi})[1-\operatorname{Re}\tilde{\Lambda}(\mathbf{k},\omega)]}\left[\omega^2-c^2k^2-\hat{\omega}^2_p+4ck\sum_{\lambda\epsilon}\frac{\bar{E}_{\mathbf{k}\lambda}|\tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2}{(\hat{E}^2_{\mathbf{k}\lambda}-\omega^2)}\right]$$

$$-\frac{2\bar{E}_{\mathbf{k}\lambda}\operatorname{Im}P_{11}}{(\omega^2-\hat{E}^2_{\mathbf{k}\lambda})[1-\operatorname{Re}\tilde{\Lambda}(\mathbf{k},\omega)]}(\omega^2-c^2k^2-\hat{\omega}^2_p)$$

$$-\frac{\operatorname{Im}(P_{11}+P_{14})}{[1-\operatorname{Re}\tilde{\Lambda}(\mathbf{k},\omega)]}\left[4ck\sum_{\lambda\epsilon}\frac{|\tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2}{(\omega^2-\hat{E}^2_{\mathbf{k}\lambda})}\right.$$

$$\left.+(\omega^2-c^2k^2-\hat{\omega}^2_p)\sum_{\lambda\xi}\frac{4\omega_{\mathbf{k}\xi}|\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2}{(\omega^2-\hat{E}^2_{\mathbf{k}\lambda})(\omega^2-\hat{\omega}^2_{\mathbf{k}\xi})}\right]. \tag{5.4c}$$

In deriving the spectral functions (5.1), only linear terms in $P(\mathbf{k},\omega)$ have been retained. In the expressions (5.2), the renormalized energies in the zero-approximation are corrected by additional self-energy terms. The excitonic energy $\bar{E}_{\mathbf{k}\lambda}$ is modified by the self-energy $\mathrm{Re}\,P_{11}(\mathbf{k},\omega)$, originating from the various anharmonic processes leading to the scattering of the exciton mode. Writing $P_{11}(\mathbf{k},\omega)$ explicitly in terms of $S_{\mathrm{ex}}(\mathbf{k},\omega)$, it can be shown that all the cubic and quartic components of the Hamiltonian, except H^3_{RRL}, contribute to the expression for $\mathrm{Re}\,P_{11}(\mathbf{k},\omega)$. There is also an off-diagonal contribution, $\mathrm{Re}\,P_{14}(\mathbf{k},\omega)$, which appears in (5.3) and (5.4). Similarly, in (5.2b) and (5.2c) the phonon and plasma frequencies are corrected by the self-energy terms, $\mathrm{Re}\,P_{33}(\mathbf{k},\omega)$ and $\mathrm{Re}\,P_{22}(\mathbf{k},\omega)$, arising from direct phonon and photon scattering processes respectively. The functions, $\theta(\mathbf{k},\omega)/(\omega^2-\hat{E}^2_{\mathbf{k}\lambda})$ and $\beta(\mathbf{k},\omega)/(\omega^2-\hat{\omega}^2_{\mathbf{k}\xi})$, where $\theta(\omega)$ and $\beta(\omega)$ are given by (5.3a) and (5.3d) respectively, are the exciton and phonon correlation functions, respectively, with anharmonic effects being included.

The square of the index of refraction is defined in (5.4a). The lattice response function (5.4b) contains anharmonic effects with both exciton and phonon energies being renormalized; the exciton-lattice coupling function $|\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2$, (3.18f), takes into account anharmonically induced interactions, which bring in the non-diagonal interaction term, $|\langle\langle S_{\mathrm{ex}}(\mathbf{k});S^\dagger_L(\mathbf{k})\rangle\rangle|^2$, even in the absence of H^1_{eL}. In (5.4a), the second term is a new contribution arising solely from anharmonicity, which describes the effect of direct photon scattering processes. The third term in (5.4a) is the usual contribution from the excitonic polarizability, modified by the lattice response function, and describes dressed (by the phonon field) polariton type excitations. The oscillator strength $|\tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2$, (3.18g), includes a non-diagonal coupling function due to anharmonicity. Hence, it can be seen that in the case where direct first-order coupling H^1_{eR} does not exist, the three fields are still coupled weakly through anharmonic interactions with induced non-diagonal coupling functions of the form $|\langle\langle S_{\mathrm{ex}}(\mathbf{k});S^\dagger_R(\mathbf{k})\rangle\rangle|^2$ and $|\langle\langle S_{\mathrm{ex}}(\mathbf{k});S^\dagger_L(\mathbf{k})\rangle\rangle|^2$, respectively. The index of refraction $\mathrm{Re}\,\tilde{\eta}^2(\mathbf{k},\omega)$ given by (5.4) can be compared with the dielectric function of Bendow and Birman [17], whose Hamiltonian is similar to ours. They have treated the exciton-lattice interaction H^1_{eL} perturbatively and hence do not obtain its influence on the polarizability represented by the lattice response function. We can recover their results from (3.17a) by incorporating the effect of H^1_{eL} into $P_{11}(\mathbf{k},\omega)$, in which only H^2_{eeL} anharmonic interaction is retained, dropping the renormalization terms and neglecting the imaginary parts of the numerator of the third term in (3.17a). Their functions [17] $\Delta(\mathbf{k}E)$ and Γ then correspond to those of $\mathrm{Re}\,P_{11}$ and $\mathrm{Im}\,P_{11}$ respectively. Therefore, Bendow and Birman's [17] expression for the dielectric constant does not include all the anharmonic effects arising from their $V^{(3)}+V^{(4)}$ and it can be viewed as a linearized form of $\tilde{\eta}(\mathbf{k},\omega)$ with the direct photon scattering processes discarded.

The damping function $\hat{\Gamma}(\mathbf{k},\omega)$ is given by (5.4c). The importance of the damping function depends entirely on the strength of the anharmonic interactions. In $\hat{\Gamma}(\mathbf{k},\omega)$, (5.4c), the first term describes the lifetime of the photon part of the polariton. Considering that $P_{22}(\mathbf{k},\omega)=\langle\langle S_R(\mathbf{k});S^\dagger_R(\mathbf{k})\rangle\rangle$ and the definition of $S_R(\mathbf{k})$ given by (3.10b), then the expression for $\mathrm{Im}\,P_{22}(\mathbf{k},\omega)$ describes direct photon scattering processes, which is present even in the absence of dispersion. The second term in (5.4c) describes the decay of the phonon part of the mode, whereas the last two terms represent the exciton contribution to $\hat{\Gamma}(\mathbf{k},\omega)$. Thus, the damping function consists of a linear combination of various decay processes arising from the interaction of the mode in question with the anharmonic parts of the three fields respectively.

We will proceed now with the evaluation of the two- and three-particle Green functions, which appear in the components $P_{ij}(\mathbf{k},\omega)$. A rigorous calculation of these Green functions can be done only through the use of the total Hamiltonian H, which is rather an impossible task. For our problem it will be sufficient to calculate the Green functions appearing in the expression for $P_{ij}(\mathbf{k},\omega)$ in the first approximation by means of the zero-order renormalized Hamiltonian

$$\mathscr{H}_{(0)}^{\text{pol}} = E_{(0)} + \sum_{\mathbf{k}\rho} \omega_{\rho(0)}(\mathbf{k})\, \gamma_{\rho(0)}^{\dagger}(\mathbf{k})\, \gamma_{\rho(0)}(\mathbf{k}). \tag{5.5}$$

In this approximation, the two- and three-particle Green functions are transformed into the new representation of dressed polariton modes and then the two- and three-dressed polariton Green functions are calculated by means of the Hamiltonian (5.5). Owing to the diagonal form of the Hamiltonian (5.5), mixed type Green functions consisting of an odd number of operators do not contribute. In this approximation, the imaginary parts of the two- and three-dressed polariton Green function have delta-function distributions respectively.

The canonical transformation which diagonalizes the Hamiltonian $H^0 + H^1$ into the dressed polariton form (5.5) is defined in (4.6), but its coefficients $u_{j\rho}^{(0)}(\mathbf{k})$ and $v_{j\rho}^{(0)}(\mathbf{k})$, $j = \lambda$, ϵ, ξ, are now calculated in the next approximation, i.e. using the zero-order renormalized Green functions. The only difference between these coefficients and those of the transformation (4.6) lies in the fact that the $u_{j\rho}^{(0)}(\mathbf{k})$ and $v_{j\rho}^{(0)}(\mathbf{k})$ contain renormalized expressions for the exciton energy and the oscillator strength.

The two- and three-dressed polariton Green functions have been calculated in the Appendix by means of the Hamiltonian (5.5) and are given by (A.3) and (A.6) respectively. It is shown that they have poles at the energies

$$\omega_1 = \pm\omega_{\rho'(0)}(\mathbf{k}') \pm \omega_{\rho''(0)}(\mathbf{k}''),$$

$$\omega_2 = \pm\omega_{\rho'(0)}(\mathbf{k}'') \pm \omega_{\rho''(0)}(\mathbf{k}'') \pm \omega_{\rho'''(0)}(\mathbf{k}'''), \tag{5.6}$$

respectively. ω_1 and ω_2 are the resonance frequencies corresponding to the first- and second-order scattering mechanisms and Equations (5.6) express the appropriate energy conservation conditions. In this same Appendix, a general form of the matrix element $P_{ij}(\mathbf{k},\omega)$ is derived. Upon expressing its coefficients $\Gamma_{\mathbf{k}\alpha}(\mathbf{k}'\rho',\ldots)$ in terms of the anharmonic coupling functions, one can see that the latter are screened by the field of the outgoing modes through the coefficients $u_{j\rho}^{(0)}(\mathbf{k})$ and $v_{j\rho}^{(0)}(\mathbf{k})$. This results in a reduction of the bare scattering amplitudes, the magnitude of which depends on the first-order coupling functions. The expression (A.8) shows further that $P_{ij}(\mathbf{k},\omega)$ is a function of the occupation numbers $n_\rho(\mathbf{k})$ of the outgoing modes and hence, is temperature dependent. Notice that in (A.8), the cubic and quartic anharmonic terms are linear and quadratic with respect to the occupation numbers respectively.

In the expressions (5.1), only the diagonal elements of $P_{ij}(\mathbf{k},\omega)$ as well as the off-diagonal element $P_{14}(\mathbf{k},\omega)$ remain as important contributions. They describe physical processes where the incoming particle (photon, or bare or dressed polariton) decays into two and three frequency modes. The scattered (or outgoing) modes can be either bare or dressed depending on the strength of the first-order interactions in the range of frequencies of the outgoing waves. Considering that when a frequency mode is dressed then its anharmonic coupling function is screened and its magnitude is reduced, therefore the decay of dressed polaritons into bare modes is more likely to occur.

The behaviour of the dressed polariton system is described by the shape functions (5.1). The exciton spectral function $\operatorname{Im} D_{\text{ex}}^{(1)}(\mathbf{k}\omega)$ is proportional to the absorption coefficient in the electronic part of the spectrum, whereas in the infrared region, the latter is proportional to the phonon spectral function $\operatorname{Im} D_L^{(1)}(\mathbf{k},\omega)$. This last function is only an approximation to the true lattice absorption since our model does not contain the lattice anharmonicity. Finally, the phonon shape function $\operatorname{Im} D_R^{(1)}(\mathbf{k},\omega)$ is proportional to the scattering probability for the electro-optic effect [18].

The functions (5.1) describing the system of three coupled fields have all the same first-order excitation spectrum with energies $\omega_{\rho(1)}(\mathbf{k})$ given by the roots of the secular equation

$$\omega^2 \operatorname{Re} \tilde{\eta}^2(\mathbf{k},\omega) - c^2 k^2 = 0 \tag{5.7a}$$

The first-order dressed polariton excitation spectrum $\omega_{\rho(1)}(\mathbf{k})$ differs from the zero-order renormalized spectrum because it contains now self-energy effects due to anharmonicity. The latter does not induce new roots of the Maxwell equation (5.7a). In the vicinity of the dressed polariton energies $\omega_{\rho(1)}(\mathbf{k})$, the equation (5.7a) can be expanded in power series and retaining the first non-vanishing term, we have

$$\sum_{\rho} \lambda_{(1)}^{-1}(\mathbf{k}\rho)\,(\omega^2 - \omega_{\rho(1)}^2(\mathbf{k}) = 0, \tag{5.7b}$$

where we have introduced the screening factor

$$\lambda_{(1)}^{-1}(\mathbf{k}\rho) = \left(\frac{d\omega^2 \operatorname{Re} \tilde{\eta}^2(\mathbf{k},\omega)}{d\omega^2}\right)_{\omega=\omega_{\rho(1)}(\mathbf{k})} = \lambda_{(1)}^{-1}(\mathbf{k},\omega_{\rho(1)}(\mathbf{k})). \tag{5.8}$$

Then, the exciton spectral function (5.1a) can be rewritten as

$$-\operatorname{Im} D_{\mathrm{ex}}^{(1)}(\mathbf{k},\omega) = \frac{1}{\pi}\sum_{\rho} \frac{\theta_s(\mathbf{k},\omega)}{(\omega^2 - \hat{E}_{\mathbf{k}\lambda}^2)} \cdot \frac{\hat{\Gamma}_s(\mathbf{k},\omega) - [\omega^2 - \omega_{\rho(1)}^2(\mathbf{k})]\,\hat{\mu}_s(\mathbf{k},\omega)/\theta_s(\mathbf{k},\omega)}{[\omega^2 - \omega_{\rho(1)}^2(\mathbf{k})]^2 + [\hat{\Gamma}_s(\mathbf{k},\omega)]^2}. \tag{5.9}$$

This expression is valid only in the neighbourhood of the excitation energies $\omega_{\rho(1)}(\mathbf{k})$. In (5.9), the subscript s affecting any function $f(\mathbf{k},\omega)$ means that this function is screened by the polarization of the medium according to the definition

$$f_s(\mathbf{k},\omega) = \lambda(\mathbf{k},\rho) f(\mathbf{k},\omega). \tag{5.10a}$$

If, furthermore, the functions $\hat{\Gamma}_s(\mathbf{k},\omega)$, $\theta_s(\mathbf{k},\omega)$ vary slowly with ω for ω close to $\omega_{\rho(1)}(\mathbf{k})$, then they can be replaced by their values $\hat{\Gamma}_s(\mathbf{k},\rho)$, $\theta_s(\mathbf{k},\rho)$ at $\omega = \omega_{\rho(1)}(\mathbf{k})$.

Then, for frequencies ω close to the energies of excitation $\omega_{\rho(1)}(\mathbf{k})$, the absorption spectrum is approximately described by the expression (5.9), whereas the shape function (5.1a) is valid throughout the entire frequency range.

The expression (5.9) consists of two terms. The first one describes a Lorentzian line

$$-\operatorname{Im} D_{\mathrm{ex}}^{(1)}(\mathbf{k};\omega) = \left(\frac{1}{\pi}\right)\frac{\theta_s(\mathbf{k},\omega)}{(\omega^2 - \hat{E}_{\mathbf{k}\lambda}^2)} \cdot \frac{\hat{\Gamma}_s(\mathbf{k},\omega)}{[\omega^2 - \omega_{\rho(1)}^2(\mathbf{k})]^2 + [\hat{\Gamma}_s(\mathbf{k},\omega)]^2}. \tag{5.10b}$$

If the frequency dependence of $\hat{\Gamma}_s(\mathbf{k},\omega)$ can be ignored, the line is symmetrically broadened and peaked at the renormalized polariton energy $\omega_{\rho(1)}(\mathbf{k})$. Its spectral width is of the order of $\hat{\Gamma}_s(\mathbf{k},\rho)$ in energy units, provided the energy $\omega_{\rho(1)}(\mathbf{k})$ satisfies one of the arguments of the δ-functions appearing in the damping function; this means that $\omega_{\rho(1)}(\mathbf{k})$ must satisfy at least one of the relations (5.6). If the frequency dependence of the damping function cannot be neglected, then the broadening of the line is asymmetric and the maximum of absorption is reached for some energy close to $\omega_{\rho(1)}(\mathbf{k})$. The smooth variation of the function $\omega^2 \operatorname{Re}\tilde{\eta}^2(\mathbf{k},\omega)$ in the absorption region results in a large screening of the damping function which is superimposed to the screening by the fields of the outgoing modes. In the limit when the damping function vanishes, which is the case when $\omega_{\rho(1)}(\mathbf{k})$ does not satisfy any of the conditions (5.6), then Equation (5.10b) has a delta function distribution, i.e.,

$$-\operatorname{Im} D_{\mathrm{ex}}^{(1)}(\mathbf{k},\omega) = \left[\frac{\theta_s(\mathbf{k},\omega)}{\omega^2 - \hat{E}_{\mathbf{k}\lambda}^2}\right] \delta(\omega^2 - \omega_{\rho(1)}^2(\mathbf{k})), \text{ for } \hat{\Gamma}_s(\mathbf{k},\omega) \to 0. \tag{5.11}$$

For frequencies, which are not solutions of the secular equation, but close to $\omega_{\rho(1)}(\mathbf{k})$, the second term of (5.9) must be considered. This term, which vanishes identically at the renormalized polariton energies $\omega_{\rho(1)}(\mathbf{k})$, contributes to the line shape for $\omega \neq \omega_{\rho(1)}(\mathbf{k})$ and results in an asymmetric broadening of the absorption band, provided that ω satisfies at least one of the arguments of the δ-functions contained in $\hat{\mu}(\mathbf{k},\omega)$ given by (5.3b). It is an anharmonic induced contribution to the exciton spectral function, linear with respect to the components of $\operatorname{Im} P_{ij}(\mathbf{k},\omega)$. The function $\hat{\mu}(\mathbf{k},\omega)$ describes the interference arising from the simultaneous presence of the three interacting fields and it will cause some asymmetry to the absorption band in the neighbourhood of frequencies $\omega_{\rho(1)}(\mathbf{k})$. It is also possible to produce side bands at the band edges of the main line at $\omega_{\rho(1)}(\mathbf{k})$. To investigate this possibility, we consider the solutions of the equation

$$\frac{d}{d\omega^2}\left[\frac{\hat{\Gamma}(\mathbf{k},\omega) - (\omega^2 \operatorname{Re}\tilde{\eta}^2(\mathbf{k},\omega) - c^2k^2)\,\hat{\mu}(\mathbf{k},\omega)/\theta(\mathbf{k},\omega)}{(\omega^2 \operatorname{Re}\tilde{\eta}^2(\mathbf{k},\omega) - c^2k^2)^2 + (\hat{\Gamma}(\mathbf{k},\omega))^2}\right] = 0. \tag{5.12a}$$

If $\nu_\mu(\mathbf{k})$ are the solutions of Equations (5.12a), we assume that near these energies the functions $\hat{\Gamma}(\mathbf{k},\nu_\mu) = \hat{\Gamma}$ and $\hat{\mu}(\mathbf{k},\nu_\mu)/\theta(\mathbf{k},\nu_\mu) = \hat{M}$ may be considered as constants, then (5.12a) gives:

$$\nu_\mu^2 \operatorname{Re}\tilde{\eta}^2(\mathbf{k},\nu_\mu) - c^2k^2 = \frac{\hat{\Gamma}}{\hat{M}}(1 \pm \sqrt{1+\hat{M}^2}). \tag{5.12b}$$

The energies $\nu_\mu(\mathbf{k})$ correspond to the excitation spectrum of the side bands, and the exciton spectral function at $\omega = \nu_\mu(\mathbf{k}) = \nu_\mu$ is

$$-\operatorname{Im} D_{\mathrm{ex}}^{(1)}(\mathbf{k},\nu_\mu) = \frac{1}{\pi}\left[\frac{\theta(\mathbf{k},\nu_\mu)}{\nu_\mu^2 - \hat{E}_{\mathbf{k}\lambda}^2}\right]\left(\frac{\hat{M}^2}{\hat{\Gamma}}\right)\cdot\frac{1}{(1 \pm \sqrt{1+\hat{M}^2})}\cdot \tag{5.12c}$$

The spectral widths of the side bands are of the order of $(\hat{\Gamma}/\hat{M}^2)(1 \pm \sqrt{1+\hat{M}^2})$. The existence of such side bands depends entirely on the value of $\hat{M}$. The present analysis indicates that asymmetric broadening of the absorption bands does not depend only on the ω dependence of $\operatorname{Re}\tilde{\eta}^2(\mathbf{k},\omega)$ and $\hat{\Gamma}(\mathbf{k},\omega)$, but also on the strength of the function $\hat{\mu}(\mathbf{k},\omega)/\theta(\mathbf{k},\omega)$.

Thus, the exciton shape function (5.1a) describes the absorption spectrum in the presence of anharmonicity, when the propagating mode is scattered into two or three outgoing particles. These scattering events lead to the decay of the renormalized polariton $\omega_{\rho(1)}(\mathbf{k})$ and are described by the damping function. $\hat{\Gamma}(\mathbf{k},\omega)$ represents the decay rate of lifetime of the renormalized polariton and is a function of the various scattering probabilities.

The photon and phonon spectral functions can be discussed in a similar fashion. Inspection of Equations (5.1) indicates that the first term is common for the three fields and, therefore, describes the same excitation spectrum. Differences occur only in the amplitudes of the corresponding spectral functions, because of the different correlation functions: $\theta(\mathbf{k},\omega)/\omega^2 - \hat{E}^2_{\mathbf{k}\lambda}$ for the exciton, ck for the photon and $\omega_{\mathbf{k}\xi}\beta(\mathbf{k},\omega)/\omega^2 - \tilde{\omega}^2_{\mathbf{k}\xi}$ for the phonon. Quantitative differences arise when the second terms are considered; the structure of the side bands is different for the three fields (5.1). This is due to the fact that the damping functions $\hat{\mu}(\mathbf{k},\omega)$, $\hat{\gamma}(\mathbf{k},\omega)$ and $\hat{\delta}(\mathbf{k},\omega)$ given by (5.3b), (5.3c) and (5.3e) respectively, consist of different scattering contributions. However, the behaviour of the photon and phonon spectral functions is similar to that of $\operatorname{Im} D^{(1)}_{\mathrm{ex}}(\mathbf{k},\omega)$ and they shall not be discussed any further.

We consider now what happens when the first-order exciton-lattice interaction H^1_{eL} vanishes. This corresponds to the limiting case b) considered in Section III. In this case the exciton and the photon fields are coupled, while the phonon field is independent. The corresponding Green functions are given by the expressions (3.23a)–(3.23c). The renormalized phonon energies are determined by the roots of Equations (3.24a), while the expression for $\operatorname{Im} P_{33}(\mathbf{k},\omega)$ describes various decay processes due to exciton-phonon and photon-phonon interactions. The behaviour of the coupled exciton-photon fields is described by the exciton and photon Green functions (2.33a) and (3.23b) respectively. Taking the imaginary part of the expression (3.23a), we have

$$-\operatorname{Im} D^{u}_{\mathrm{ex}}(\mathbf{k},\omega) = \frac{1}{\pi}\left[\frac{\theta_u(\mathbf{k},\omega)}{\omega^2 - \hat{E}^2_{\mathbf{k}\lambda}}\right]\frac{\hat{\Gamma}_u(\mathbf{k},\omega) - [\omega^2 \operatorname{Re}\tilde{\eta}^2_u(\mathbf{k},\omega) - c^2k^2]\,\hat{\mu}_u(\mathbf{k},\omega)/\theta_u(\mathbf{k},\omega)}{[\omega^2 \operatorname{Re}\tilde{\eta}^2_u(\mathbf{k},\omega) - c^2k^2]^2 + [\hat{\Gamma}_u(\mathbf{k},\omega)]^2}, \tag{5.13}$$

where

$$\theta_u(\mathbf{k},\omega) = (\hat{E}_{\mathbf{k}\lambda} + \operatorname{Re} P_{14})(\omega^2 - c^2k^2 - \hat{\omega}^2_p), \tag{5.14a}$$

$$\hat{\mu}_u(\mathbf{k},\omega) = (\omega^2 - c^2k^2 - \hat{\omega}^2_p)\operatorname{Im}(P_{11} + P_{14}) - (\hat{E}_{\mathbf{k}\lambda} + \operatorname{Re} P_{14})\operatorname{Im} P_{22}, \tag{5.14b}$$

$$\begin{aligned}\hat{\Gamma}_u(\mathbf{k},\omega) = &-\operatorname{Im} P_{22} - \left[\frac{2\bar{E}_{\mathbf{k}\lambda}\operatorname{Im} P_{11}}{\omega^2 - \hat{E}^2_{\mathbf{k}\lambda}}\right](\omega^2 - c^2k^2 - \omega^2_p)\\ &- 4ck\sum_{\lambda\epsilon}\frac{|\tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2}{(\omega^2 - \hat{E}^2_{\mathbf{k}\lambda})}\operatorname{Im}(P_{11} + P_{14}),\end{aligned} \tag{5.14c}$$

$$\operatorname{Re}\tilde{\eta}^2_u(\mathbf{k},\omega) = 1 - \frac{\hat{\omega}^2_p}{\omega^2} - \frac{4ck}{\omega^2}\sum_{\lambda\epsilon}\frac{|\tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2}{(\omega^2 - \hat{E}^2_{\mathbf{k}\lambda})}(\hat{E}_{\mathbf{k}\lambda} + \operatorname{Re} P_{14}). \tag{5.14d}$$

The polariton excitation spectrum is given by the roots $\omega^u_{\rho(1)}(\mathbf{k})$ of the secular equation

$$\omega^2 \operatorname{Re}\tilde{\eta}^2_u(\mathbf{k},\omega) - c^2k^2 = 0. \tag{5.15}$$

In this case, the polariton and phonon fields are independent of one another and, therefore, the truncated Hamiltonian (5.5) becomes

$$\mathscr{H}_{(0)} = \bar{E}_{(0)} + \sum_{\mathbf{k}\rho}\omega^u_{\rho(0)}(\mathbf{k})\,\gamma^{u\dagger}_{\rho(0)}(\mathbf{k})\,\gamma^u_{\rho(0)}(\mathbf{k}) + \sum_{\mathbf{k}\xi}\omega_{\mathbf{k}\xi}(b^\dagger_{\mathbf{k}\xi}b_{\mathbf{k}\xi} + \tfrac{1}{2}). \tag{5.16}$$

This Hamiltonian can be used to calculate the two- and three-particle Green functions contained in the expressions for $P_{ij}(\mathbf{k},\omega)$ in a similar fashion to that used previously. The polariton operators $\gamma^{u}_{\rho(0)}(\mathbf{k})$ and $\gamma^{u\dagger}_{\rho(0)}(\mathbf{k})$ consist of an admixture of exciton and photon operators only.

Since the expression (5.13) can be derived from (5.1a) when the limit $g_{\mathbf{k}\xi}(\mathbf{k}\lambda) \to 0$ is taken, both expressions describe similar excitation spectra. The difference is that the function (5.1a) is more appropriate to describe the spectrum of polar crystals than the expression (5.13). Therefore, the previous analysis for the dressed polariton spectrum is applicable here for the bare polariton with the understanding of $\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda) \to 0$. The poles of all matrix elements $P_{ij}(\mathbf{k},\omega)$ in the representation of (5.16) are located at the energies:

$$\begin{aligned} \omega_{1a} &= \pm\omega^{u}_{\rho'(0)}(\mathbf{k}') \pm \omega^{u}_{\rho''(0)}(\mathbf{k}''), \\ \omega_{1b} &= \pm\omega^{u}_{\rho'(0)}(\mathbf{k}') \pm \omega_{\mathbf{k}''\xi''}, \\ \omega_{1c} &= \pm\omega_{\mathbf{k}'\xi'} \pm \omega_{\mathbf{k}''\xi''}, \end{aligned} \tag{5.17}$$

(corresponding to polariton-polariton, polariton-phonon and phonon-phonon decay mechanisms respectively) for the first-order scattering, and four similar combinations of three energies for the second-order scattering (three-particle decay processes). The energy conservation conditions (5.17) indicate that the incoming polariton may decay into two polaritons, one polariton and one phonon or two phonons respectively.

Let us consider now the case where the electromagnetic field suffers no dispersion, i.e., $|\tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2 = 0$, while the exciton and the phonon fields are coupled and the corresponding Green functions are given by (3.21). The spectral functions for the bare photon and dressed exciton fields are found to be

$$- \operatorname{Im} D^{b}_{\mathrm{ex}}(\mathbf{k},\omega) = \left(\frac{1}{\pi}\right)\cdot\left(\frac{\theta^{b}(\mathbf{k},\omega)}{\omega^2 - \hat{E}^2_{\mathbf{k}\lambda}}\right)$$

$$\cdot\frac{\hat{\Gamma}^{b}(\mathbf{k},\ \omega) - [1 - \operatorname{Re}\ \tilde{\Lambda}(\mathbf{k},\ \omega)]\ \hat{\mu}^{b}(\mathbf{k},\ \omega)/\theta^{b}(\mathbf{k},\ \omega)}{[(1 - \operatorname{Re}\tilde{\Lambda}(\mathbf{k},\omega)]^2 + [\hat{\Gamma}^{b}(\mathbf{k},\omega)]^2}, \tag{5.18a}$$

$$- \operatorname{Im} D^{b}_{L}(\mathbf{k},\omega) = \left(\frac{\omega_{\mathbf{k}\xi}}{\pi}\right)\cdot\frac{\hat{\Gamma}^{b}(\mathbf{k},\omega) - [1 - \operatorname{Re}\tilde{\Lambda}(\mathbf{k},\omega)]\,\hat{\delta}^{b}(\mathbf{k},\omega)}{[1 - \operatorname{Re}\tilde{\Lambda}(\mathbf{k},\omega)]^2 + [\hat{\Gamma}^{b}(\mathbf{k},\omega)]^2}, \tag{5.18b}$$

$$- \operatorname{Im} D^{b}_{R}(\mathbf{k},\omega) = \left(\frac{ck}{\pi}\right)\cdot\frac{\operatorname{Im} P_{22}}{(\omega^2 - c^2k^2 - \hat{\omega}^2_p)^2 + (\operatorname{Im} P_{22})^2}. \tag{5.18c}$$

Use has been made of the notation:

$$\theta^{b}(\mathbf{k},\omega) = \hat{E}_{\mathbf{k}\lambda} + \operatorname{Re} P_{14}, \tag{5.19a}$$

$$\hat{\mu}^{b}(\mathbf{k},\omega) = \operatorname{Im}(P_{11} + P_{14}) - (\hat{E}_{\mathbf{k}\lambda} + \operatorname{Re} P_{14})\,\frac{\operatorname{Im} P_{33}}{(\omega^2 - \hat{\omega}^2_{\mathbf{k}\xi})}, \tag{5.19b}$$

$$\hat{\delta}^{b}(\mathbf{k},\omega) = 2\bar{E}_{\mathbf{k}\lambda}\left(\frac{\operatorname{Im} P_{11}}{\hat{E}^2_{\mathbf{k}\lambda} - \omega^2}\right), \tag{5.19c}$$

$$\hat{\Gamma}^b(\mathbf{k},\omega) = 2\bar{E}_{\mathbf{k}\lambda}\left(\frac{\operatorname{Im} P_{11}}{\hat{E}^2_{\mathbf{k}\lambda}-\omega^2}\right) - \left(\frac{\operatorname{Im} P_{33}}{\omega^2-\hat{\omega}^2_{\mathbf{k}\xi}}\right) - \sum_{\lambda\xi}\frac{4\omega_{\mathbf{k}\xi}|\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2\operatorname{Im}(P_{11}+P_{14})}{(\omega^2-\hat{E}^2_{\mathbf{k}\lambda})(\omega^2-\hat{\omega}^2_{\mathbf{k}\xi})}, \tag{5.19d}$$

and the expression for 1-Re$\tilde{\Lambda}(\mathbf{k},\omega)$ is given by (5.4b). The expression (5.18a) represents the coupled exciton and phonon fields and is appropriate to describe the excitation spectrum of polar crystals, when the oscillator strength for the corresponding optical transition is extremely small.

The photon shape function (5.18c) is a Lorentzian line centred around the photon excitation energy $(c^2k^2+\hat{\omega}_p^2)^{\frac{1}{2}} = \omega_R(\mathbf{k})$ and having an energy width of the order of Im P_{22}. The damping function Im P_{22} describes various scattering events leading to the decay of the incoming photon. On the other hand, both the exciton and phonon spectral functions are made of the superposition of two terms. The first term describes Lorentzian lines peaked at or near the dressed exciton energies $\omega^b_{\rho(1)}(\mathbf{k})$, which are determined by the roots of the equation 1-Re$\tilde{\Lambda}(\mathbf{k},\omega)=0$. The broadening of the main line is governed by the dressed exciton damping function $\hat{\Gamma}^b(\mathbf{k},\omega)$. The second term vanishes identically at the dressed exciton energies $\omega^b_{\rho(1)}(\mathbf{k})$, but causes an asymmetric broadening for frequencies ω different than $\omega^b_{\rho(1)}(\mathbf{k})$. In general, broadening of the absorption spectrum occurs provided that the following energy conservation conditions are obeyed

$$\begin{aligned}
\omega_{1a} &= \pm\omega^b_{\rho'(0)}(\mathbf{k}') \pm \omega^b_{\rho''(0)}(\mathbf{k}''),\\
\omega_{1b} &= \pm\omega^b_{\rho'(0)}(\mathbf{k}') \pm \omega_R(\mathbf{k}''),\\
\omega_{1c} &= \pm\omega_R(\mathbf{k}') \pm \omega_R(\mathbf{k}'')
\end{aligned} \tag{5.20}$$

(corresponding to dressed exciton-exciton, dressed exciton-photon and photon-photon scattering processes respectively). Similar relations hold for the three-particle scattering processes. The conditions (5.20) are also valid for Im P_{22} and they indicate that the incoming photon or the dressed exciton may decay into various combinations of photon and dressed exciton modes. In the expression for Im P_{22}, the condition ω_{1b} is associated with the Raman scattering of photons by dressed excitons.

Finally, when the three fields are independent of each other, i.e., $|\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2 = |\tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2 = 0$, the spectral function for the photon field remains the same (5.18c), while those of the exciton and phonon fields are decoupled and given by

$$-\operatorname{Im} D^F_{\mathrm{ex}}(\mathbf{k},\omega) = \left(\frac{1}{\pi}\right)\cdot\frac{(\hat{E}_{\mathbf{k}\lambda}+\operatorname{Re}P_{14})\,2\bar{E}_{\mathbf{k}\lambda}\operatorname{Im}P_{11} + (\omega^2-\hat{E}^2_{\mathbf{k}\lambda})\operatorname{Im}(P_{11}+P_{14})}{(\omega^2-\hat{E}^2_{\mathbf{k}\lambda})^2 + (2\bar{E}_{\mathbf{k}\lambda}\operatorname{Im}P_{11})^2}, \tag{5.18a}$$

$$-\operatorname{Im} D^F_L(\mathbf{k},\omega) = \left(\frac{\omega_{\mathbf{k}\xi}}{\pi}\right)\cdot\frac{\operatorname{Im}P_{33}}{(\omega^2-\hat{\omega}^2_{\mathbf{k}\xi})^2+(\operatorname{Im}P_{33})^2}. \tag{5.18b}$$

In the infrared region of the spectrum, the absorption coefficient is proportional to Im $D^F_L(\mathbf{k},\omega)$, which consists of Lorentzian lines located around the frequencies $\hat{\omega}_{\mathbf{k}\xi}$. In the visible region of frequencies, the spectrum is governed by Im $D^F_{\mathrm{ex}}(\mathbf{k},\omega)$, which consists of the superposition of Lorentzian lines peaked at or near $\hat{E}_{\mathbf{k}\lambda}$ and of asymmetric broad bands, provided the appropriate energy conservation conditions are satisfied. The latter are now made of all possible combinations of two and three bare exciton, phonon and photon energies. The components of $P_{ij}(\mathbf{k},\omega)$ may be calculated now by means of the unperturbed Hamiltonian H^0 (2.2a).

In considering the specific physical processes, where the exciton photon and phonon fields are decoupled, we have made the assumption that the anharmonically induced contributions given by the last term of Equations (3.18f) and (3.18g) respectively are negligibly small. These terms may be of some importance in the absence of first-order interactions between the fields. They consist of the non-diagonal matrix elements of $P_{ij}(\mathbf{k}, \omega)$, i.e.,

$$P_{12}(\mathbf{k}, \omega) = \left(\frac{1}{2\pi}\right) \langle\langle S_{\mathrm{ex}}(\mathbf{k}); S_R^\dagger(\mathbf{k})\rangle\rangle,$$

$$P_{13}(\mathbf{k}, \omega) = \left(\frac{1}{2\pi}\right) \langle\langle S_{\mathrm{ex}}(\mathbf{k}); S_L^\dagger(\mathbf{k})\rangle\rangle$$

and

$$P_{23}(\mathbf{k}, \omega) = \left(\frac{1}{2\pi}\right) \langle\langle S_R(\mathbf{k}); S_L^\dagger(\mathbf{k})\rangle\rangle.$$

However, when the Green functions that appear in these expressions are evaluated, say, through H^0, the derived non-vanishing expressions are extremely small. Therefore, they should be considered only whenever they make substantial contributions, which may be the case when the first-order interactions vanish (from symmetry considerations) in the presence of strong anharmonicity.

VI. Raman Scattering

As has been shown in the preceding section, the damping function $\hat{\Gamma}(\mathbf{k}, \omega)$, (5.4c), describes the broadening of the absorption band arising from physical processes, where the dressed polariton decays into two and three particles. Therefore, it represents the decay rate of the particular mode and is a function of the various scattering probabilities due to anharmonicity. Using the expression (5.4c) we rewrite the decay rate in the form

$$\begin{aligned}\hat{\Gamma}(\mathbf{k}, \omega) = -\Bigg[& \operatorname{Im} P_{22}(\mathbf{k}, \omega) + \frac{4ck \operatorname{Re} \tilde{\alpha}(\mathbf{k}, \omega)}{[1 - \operatorname{Re} \tilde{\Lambda}(\mathbf{k}, \omega)]^2} \left(\frac{2\hat{E}_{\mathbf{k}\lambda}}{\hat{E}_{\mathbf{k}\lambda}^2 - \omega^2}\right) \operatorname{Im} P_{11}(\mathbf{k}, \omega) \\ & - \frac{4ck \operatorname{Re} \tilde{\alpha}(\mathbf{k}, \omega)}{[1 - \operatorname{Re} \tilde{\Lambda}(\mathbf{k}, \omega)^2]} \cdot \frac{\operatorname{Im}[P_{11}(\mathbf{k}, \omega) + P_{14}(\mathbf{k}, \omega)]}{\hat{E}_{\mathbf{k}\lambda}} \\ & + \frac{4ck \operatorname{Re} \tilde{\alpha}(\mathbf{k}, \omega) \operatorname{Re} \tilde{\Lambda}(\mathbf{k}, \omega)}{[1 - \operatorname{Re} \tilde{\Lambda}(\mathbf{k}, \omega)]^2} \cdot \frac{\operatorname{Im} P_{33}(\mathbf{k}, \omega)}{(\hat{\omega}_{\mathbf{k}\xi}^2 - \omega^2)}\Bigg], \end{aligned} \tag{6.1}$$

where $(\mathbf{k}, \omega)$ refers to the incoming particle and use has been made of the notation:

$$\operatorname{Re} \tilde{\alpha}(\mathbf{k}, \omega) = \sum_{\lambda\epsilon} \frac{|\tilde{f}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2 (\hat{E}_{\mathbf{k}\lambda} + \operatorname{Re} P_{14})}{(\hat{E}_{\mathbf{k}\lambda}^2 - \omega^2)}.$$

The expression (6.1) is a linear combination of the damping functions $\operatorname{Im} P_{ij}$, the components of which represent the anharmonic parts of the three fields that interact with the frequency mode in question. The coefficients of the linear combination in (6.1) connecting the various scattering probabilities can be expressed in terms of amplitudes $u_{j\rho}^{(1)}(\mathbf{k})$ and $v_{j\rho}^{(1)}(\mathbf{k})$ of the canonical transformation, which diagonalize the

Hamiltonian into the dressed polariton representation. The decay rate can be, therefore, written in the form

$$\hat{\Gamma}(\mathbf{k}\rho) = -\omega^{-1}_{\rho(1)}(\mathbf{k})\,\lambda^{-1}_{(1)}(\mathbf{k}\rho)\Bigg[|u^{(1)}_{\epsilon\rho}(\mathbf{k}) + v^{(1)}_{\epsilon\rho}(\mathbf{k})|^2\,\frac{\operatorname{Im} P_{22}}{ck} + |u^{(1)}_{\xi\rho}(\mathbf{k}) + v^{(1)}_{\xi\rho}(\mathbf{k})|^2\,\frac{\operatorname{Im} P_{33}}{\omega_{\mathbf{k}\xi}}$$
$$+ |u^{(1)}_{\lambda\rho}(\mathbf{k}) - v^{(1)}_{\lambda\rho}(\mathbf{k})|^2\,\frac{[\bar{E}^2_{\mathbf{k}\lambda} + \omega^2(\mathbf{k})]}{\bar{E}^2_{\mathbf{k}\lambda}}\operatorname{Im} P_{11} - |u^{(1)}_{\lambda\rho}(\mathbf{k}) - v^{(1)}_{\lambda\rho}(\mathbf{k})|^2\,\frac{[\bar{E}^2_{\mathbf{k}\lambda} - \omega^2_{\rho}(\mathbf{k})]}{\bar{E}^2_{\mathbf{k}\lambda}}\operatorname{Im} P_{14}\Bigg], \tag{6.2}$$

where ρ is the branch index of the dressed polariton and the screening factor

$$\lambda^{-1}_{(1)}(\mathbf{k}\rho) = \left(\frac{d\omega^2 \operatorname{Re}\tilde{\eta}^2(\mathbf{k},\omega)}{d\omega^2}\right)_{\omega=\omega_{\rho(1)}(\mathbf{k})}$$

represents the polarization of the medium. Considering that in the spectral function (5.9), which is valid in the vicinity of the polariton energy, the damping function is screened and, hence, the factor $\lambda^{-1}_{(1)}(\mathbf{k}\rho)$ that appears in (6.2) cancels out. In the last term of (6.2), the small off-diagonal component $\operatorname{Im}P_{14}$ is multiplied by a small coefficient so that its contribution can be considered as negligible.

A general expression for $P_{ij}(\mathbf{k},\omega)$ is given in the Appendix, calculated in the harmonic approximation for dressed polaritons. In (A.8), the first sum represents the decay into two outgoing modes and its imaginary part gives the first-order scattering probabilities. The first term in (A.8) is multiplied by the factor $(1 + n_{\rho'}(\mathbf{k}') + n_{\rho''}(\mathbf{k}''))$, where $n_{\rho'}(\mathbf{k}')$ and $n_{\rho''}(\mathbf{k}'')$ are the average values of the occupation numbers of the outgoing particles and represents the Stokes component, whereas the anti-Stokes part is multiplied by the difference between the occupation numbers. The latter is a thermal effect which vanishes in the limit of zero temperature. The second and third sum in (A.8) represent the decay into three outgoing modes and give the second-order scattering amplitudes. The last term is a contribution to the second-order scattering, where two of the outgoing polaritons having the same band index ρ and wave-vectors $\mathbf{k}$, but opposite energies cancel one another. It is a small static self-energy correction arising from quartic anharmonicity and will be discarded. The second-order scattering contribution can be divided into two parts, which behave differently as functions of the temperature. The first one is multiplied by the factor

$$[1 + n_{\rho'}(\mathbf{k}')][1 + n_{\rho''}(\mathbf{k}'') + n_{\rho'''}(\mathbf{k}''')] + n_{\rho''}(\mathbf{k}'')\,n_{\rho'''}(\mathbf{k}''')$$

and is the second order analogous of the Stokes component, which does not vanish in the limit of zero temperature. The second contribution is made of three terms which are multiplied by $n_{\rho'}(\mathbf{k}')[1 + n_{\rho''}(\mathbf{k}'') + n_{\rho'''}(\mathbf{k}''')] - n_{\rho''}(\mathbf{k}'')\,n_{\rho'''}(\mathbf{k}''')$ and which clearly represent thermal effects like the anti-Stokes component.

In the expression for $\operatorname{Im} P_{ij}(\mathbf{k},\omega)$, and hence in (6.2), the summations run all over the wave-vectors of the outgoing modes and branch indices to give the total decay rate of the incoming polariton. From this, we obtain the probability for the processes where the incoming mode decays into two or three outgoing polaritons $(\mathbf{k}'\rho')$, $(\mathbf{k}''\rho'')$ and $(\mathbf{k}'''\rho''')$, which is proportional to the first- or second-order scattering cross section.

(a) First-order scattering

Using (A.8) and (6.2) together with the definitions of the components $P_{ij}(\mathbf{k},\omega)$ and taking the expression for the u's and v's for the incoming polariton in the zero-order renormalized approximation, for the sake of consistency, we write then the probability for the Stokes process where the polariton $(\mathbf{k}\rho)$ decays into $(\mathbf{k}'\rho')$ and $(\mathbf{k}''\rho'')$ as

$$\begin{aligned} W^{s}_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\rho'') = \omega_{\rho(0)}(\mathbf{k})\,\lambda_0^{-1}(\mathbf{k}\rho)\Big[&|u^{(0)}_{\epsilon\rho}(\mathbf{k})+v^{(0)}_{\epsilon\rho}(\mathbf{k})|^2 R_{\mathbf{k}\epsilon}(\mathbf{k}'\rho',\mathbf{k}''\rho'')\\ &+|u^{(0)}_{\xi\rho}(\mathbf{k})+v^{(0)}_{\xi\rho}(\mathbf{k})|^2 R_{\mathbf{k}\xi}(\mathbf{k}'\rho',\mathbf{k}''\rho'')\\ &+|u^{(0)}_{\lambda\rho}(\mathbf{k})-v^{(0)}_{\lambda\rho}(\mathbf{k})|^2 R_{\mathbf{k}\lambda}(\mathbf{k}'\rho',\mathbf{k}''\rho'')\Big]\times[1+n_{\rho'}(\mathbf{k}')\\ &+n_{\rho''}(\mathbf{k}'')]\,\delta_{\mathbf{k}'-\mathbf{k}'',\mathbf{k}}\,\delta(\omega_{\rho(0)}(\mathbf{k}')-\omega_{\rho'(0)}(\mathbf{k}')-\omega_{\rho''(0)}(\mathbf{k}'')), \end{aligned} \tag{6.3}$$

where we have made the following definitions:

$$\begin{aligned} R_{\mathbf{k}\epsilon}(\mathbf{k}'\rho',\mathbf{k}''\rho'') = \Big|&\sum_{\lambda'\lambda''}[u^{(0)}_{\lambda'\rho'}(\mathbf{k}')\,v^{(0)}_{\lambda''\rho''}(\mathbf{k}'')+v^{(0)}_{\lambda'\rho'}(\mathbf{k}')\,u^{(0)}_{\lambda''\rho''}(\mathbf{k}'')]\times[F_{-\mathbf{k}\epsilon}(\mathbf{k}'\lambda',\mathbf{k}''\lambda'')\\ &+F^{*}_{-\mathbf{k}\epsilon}(\mathbf{k}''\lambda'',\mathbf{k}'\lambda')]+\sum_{\epsilon'\xi''}[u^{(0)}_{\epsilon'\rho'}(\mathbf{k}')+v^{(0)}_{\epsilon'\rho'}(\mathbf{k}')][u^{(0)}_{\xi''\rho''}(\mathbf{k}'')\\ &+v^{(0)}_{\xi''\rho''}(\mathbf{k}'')][\phi_{\mathbf{k}''\xi''}(\mathbf{k}'\epsilon',-\mathbf{k}\epsilon)+\phi_{\mathbf{k}''\xi''}(\mathbf{k}\epsilon,-\mathbf{k}'\epsilon')]+\sum_{\epsilon''\xi'}[u^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')\\ &+v^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')][u^{(0)}_{\xi'\rho'}(\mathbf{k}')+v^{(0)}_{\xi'\rho'}(\mathbf{k}')][\phi_{\mathbf{k}'\xi'}(\mathbf{k}''\epsilon'',-\mathbf{k}\epsilon)+\phi_{\mathbf{k}'\xi'}(\mathbf{k}\epsilon,-\mathbf{k}''\epsilon'')]\Big|^2\\ +\Big|&\sum_{\lambda'\xi''}[u^{(0)}_{\lambda'\rho'}(\mathbf{k}')-v^{(0)}_{\lambda'\rho'}(\mathbf{k}')][u^{(0)}_{\xi''\rho''}(\mathbf{k}'')+v^{(0)}_{\xi''\rho''}(\mathbf{k}'')]\,\theta_{\mathbf{k}''\xi''}(\mathbf{k}'\lambda',-\mathbf{k}\epsilon)\\ &+\sum_{\lambda''\xi'}[u^{(0)}_{\lambda''\rho''}(\mathbf{k}'')-v^{(0)}_{\lambda''\rho''}(\mathbf{k}'')][u^{(0)}_{\xi'\rho'}(\mathbf{k}')+v^{(0)}_{\xi'\rho'}(\mathbf{k}')]\,\theta_{\mathbf{k}'\xi'}(\mathbf{k}''\lambda'',-\mathbf{k}\epsilon)\Big|^2, \end{aligned} \tag{6.4a}$$

$$\begin{aligned} R_{\mathbf{k}\xi}(\mathbf{k}'\rho',\mathbf{k}''\rho'') = \Big|&\sum_{\lambda'\lambda''}[u^{(0)}_{\lambda'\rho'}(\mathbf{k}')\,v^{(0)}_{\lambda''\rho''}(\mathbf{k}'')+u^{(0)}_{\lambda''\rho''}(\mathbf{k}'')\,v^{(0)}_{\lambda'\rho'}(\mathbf{k}')]\times[G_{-\mathbf{k}\xi}(\mathbf{k}'\lambda',\mathbf{k}''\lambda'')\\ &+G^{*}_{-\mathbf{k}\xi}(\mathbf{k}''\lambda'',\mathbf{k}'\lambda')]+\sum_{\epsilon'\epsilon''}[u^{(0)}_{\epsilon'\rho'}(\mathbf{k}')+v^{(0)}_{\epsilon'\rho'}(\mathbf{k}')][u^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')\\ &+v^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')][\phi_{-\mathbf{k}\xi}(\mathbf{k}'\epsilon',\mathbf{k}''\epsilon'')+\phi^{*}_{-\mathbf{k}\xi}(\mathbf{k}''\epsilon'',\mathbf{k}'\epsilon')]\Big|^2\\ +\Big|&\sum_{\lambda'\xi''}[u^{(0)}_{\lambda'\rho'}(\mathbf{k}')-v^{(0)}_{\lambda'\rho'}(\mathbf{k}')][u^{(0)}_{\xi''\rho''}(\mathbf{k}'')+v^{(0)}_{\xi''\rho''}(\mathbf{k}'')][d_{\mathbf{k}''\xi''-\mathbf{k}\xi}(\mathbf{k}'\lambda')\\ &+d_{-\mathbf{k}\xi\mathbf{k}''\xi''}(\mathbf{k}'\lambda')]+\text{interch.}+\sum_{\lambda'\epsilon''}[u^{(0)}_{\lambda'\rho'}(\mathbf{k}')-v^{(0)}_{\lambda'\rho'}(\mathbf{k}')][u^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')\\ &+v^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')]\,\theta_{-\mathbf{k}\xi}(\mathbf{k}'\lambda',\mathbf{k}''\epsilon'')+\text{interch.}\Big|^2, \end{aligned} \tag{6.4b}$$

$$\begin{aligned} R_{\mathbf{k}\lambda}(\mathbf{k}'\rho',\mathbf{k}''\rho'') = \Big|&\sum_{\lambda'\xi''}u^{(0)}_{\lambda'\rho'}(\mathbf{k}')[u^{(0)}_{\xi''\rho''}(\mathbf{k}'')+v^{(0)}_{\xi''\rho''}(\mathbf{k}'')]\,G_{\mathbf{k}''\xi''}(\mathbf{k}\lambda,\mathbf{k}'\lambda')+\text{interch.}\\ &+\sum_{\lambda'\epsilon''}u^{(0)}_{\lambda'\rho'}(\mathbf{k}')[u^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')+v^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')][F_{\mathbf{k}''\epsilon''}(\mathbf{k}\lambda,\mathbf{k}'\lambda'+F^{*}_{\mathbf{k}''\epsilon''}(\mathbf{k}'\lambda',\mathbf{k}\lambda)]\\ &+\text{interch.}+\sum_{\xi'\xi''}[u^{(0)}_{\xi'\rho'}(\mathbf{k}')+v^{(0)}_{\xi'\rho'}(\mathbf{k}')][u^{(0)}_{\xi''\rho''}(\mathbf{k}'')\\ &+v^{(0)}_{\xi''\rho''}(\mathbf{k}'')][d_{\mathbf{k}'\xi'\mathbf{k}''\xi''}(\mathbf{k}\lambda)+d_{\mathbf{k}''\xi''\mathbf{k}'\xi'}(\mathbf{k}\lambda)]+\sum_{\xi'\epsilon''}[u^{(0)}_{\xi'\rho'}(\mathbf{k}')\\ &+v^{(0)}_{\xi'\rho'}(\mathbf{k}')][u^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')+v^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')]\,\theta_{\mathbf{k}'\xi'}(\mathbf{k}\lambda,\mathbf{k}''\epsilon'')+\text{interch.}\Big|^2, \end{aligned} \tag{6.4c}$$

$$n_\rho(\mathbf{k}) = \langle\gamma^{\dagger}_{\rho}(\mathbf{k})\,\gamma_\rho(\mathbf{k})\rangle. \tag{6.5}$$

The coefficients of the canonical transformation are given by

$$|u^{(0)}_{\epsilon'\rho'}(\mathbf{k}') + v^{(0)}_{\epsilon'\rho'}(\mathbf{k}')| = \left(\frac{ck'}{\omega_{\rho'(0)}(\mathbf{k}')}\right)^{\frac{1}{2}} \lambda_0^{\frac{1}{2}}(\mathbf{k}'\rho'),$$

$$|u^{(0)}_{\xi'\rho'}(\mathbf{k}') + v^{(0)}_{\xi'\rho'}(\mathbf{k}')| = \left(\frac{\lambda_0(\mathbf{k}'\rho')}{\omega_{\rho'(0)}(\mathbf{k}')}\right)^{\frac{1}{2}} \left(\frac{\omega_{\mathbf{k}'\xi'}}{\omega^2_{\mathbf{k}'\xi'} - \omega^2_{\rho'(0)}(\mathbf{k}')}\right)^{\frac{1}{2}} \frac{[4ck'\,\alpha_0(\mathbf{k}'\rho')\,\Lambda_0(\mathbf{k}'\rho')]^{\frac{1}{2}}}{[1-\Lambda_0(\mathbf{k}'\rho')]},$$

$$|u^{(0)}_{\lambda'\rho'}(\mathbf{k}')| = \tfrac{1}{2}\left(\frac{\lambda_0(\mathbf{k}'\rho')}{\omega_{\rho'(0)}(\mathbf{k}')}\right)^{\frac{1}{2}} \left(\frac{\bar{E}_{\mathbf{k}'\lambda'}}{\bar{E}^2_{\mathbf{k}'\lambda'} - \omega^2_{\rho'(0)}(\mathbf{k}')}\right)^{\frac{1}{2}} \frac{[4ck'\,\alpha_0(\mathbf{k}'\rho')]^{\frac{1}{2}}}{[1-\Lambda_0(\mathbf{k}'\rho')]} \left(\frac{\omega_{\rho'(0)}(\mathbf{k}')}{\bar{E}_{\mathbf{k}'\lambda'}} + 1\right),$$

$$|v^{(0)}_{\lambda'\rho'}(\mathbf{k}')| = \tfrac{1}{2}\left(\frac{\lambda_0(\mathbf{k}'\rho')}{\omega_{\rho'(0)}(\mathbf{k}')}\right)^{\frac{1}{2}} \left(\frac{\bar{E}_{\mathbf{k}'\lambda'}}{\bar{E}^2_{\mathbf{k}'\lambda'} - \omega^2_{\rho'(0)}(\mathbf{k}')}\right)^{\frac{1}{2}} \frac{[4ck'\,\alpha_0(\mathbf{k}'\rho')]^{\frac{1}{2}}}{[1-\Lambda_0(\mathbf{k}'\rho')]} \left(\frac{\omega_{\rho'(0)}(\mathbf{k}')}{\bar{E}_{\mathbf{k}'\lambda'}} - 1\right). \tag{6.6}$$

The dressed polariton scattering probability (6.3) is expressed in terms of the functions (6.4a), (6.4b) and (6.4c), which represent contributions to the total probability arising from the cubic anharmonic parts of the photon, phonon and exciton fields respectively. Owing to the symmetry of the dressed polariton representation, the amplitudes (6.3) and (6.4) are fully symmetric with respect to the interchange of the outgoing modes. The interchange between the two modes has been considered explicitly in amplitude (6.4a), while it is indicated by 'interch.' in the expressions (6.4b) and (6.4c) for the sake of convenience.

In the expression (6.3), $\delta_{\mathbf{k}'-\mathbf{k}'',\mathbf{k}}$ indicates the usual wave-vector conservation condition, whereas the delta function $\delta(\omega_{\rho(0)}(\mathbf{k}) - \omega_{\rho'(0)}(\mathbf{k}') - \omega_{\rho''(0)}(\mathbf{k}''))$ expresses the well-known energy conservation condition. The latter arises from the fact that the two-particle Green functions have been calculated using the truncated dressed polariton Hamiltonian (5.5), which physically indicates that the scattered modes are independent of one another. This approximation is sufficient provided that there are no divergent terms in the expression (6.3). If the scattered modes interact or interfere with each other, then the approximation (6.3) is not adequate. In such a case, one has to use the complete Hamiltonian for the evaluation of the Green functions that appear in the expression for $P_{ij}(\mathbf{k},\omega)$. Such a procedure will result in replacing the delta function in (6.3) by a shape function, which will describe the interaction between the scattered modes. We shall limit ourselves here to the approximation (6.3). The total amplitude $W^s_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\rho'')$ is temperature dependent through the occupation numbers and the expressions for the $u^{(0)}$'s and $v^{(0)}$'s. In the expression (6.3) the bare anharmonic coupling functions are screened by the field of the outgoing modes and, in the vicinity of the excitation energy, by that of the incoming mode.

Upon introducing the phase velocity

$$v_{p(0)}(\mathbf{k}\rho) = \mathbf{k}^{-1}\,\omega_{\rho(0)}(\mathbf{k}), \tag{6.7a}$$

and the relation between the energy transport velocity [16] $v_{E(0)}(\mathbf{k}\rho)$ and the screening factor $\lambda_0^{-1}(\mathbf{k}\rho)$

$$\lambda_0^{-1}(\mathbf{k}\rho) = \left(\frac{d\omega^2\,\eta_0^2(\mathbf{k},\omega)}{d\omega^2}\right)_{\omega=\omega_{\rho(0)}(\mathbf{k})} = \frac{c^2}{v_{p(0)}(\mathbf{k}\rho)\,v_{E(0)}(\mathbf{k}\rho)}, \tag{6.7b}$$

the partial amplitudes in (6.4) can be rewritten and the factor

$$\frac{ck'\lambda_0(\mathbf{k}'\rho')}{\omega_{\rho'(0)}(\mathbf{k}')}\cdot\frac{ck''\lambda_0(\mathbf{k}''\rho'')}{\omega_{\rho''(0)}(\mathbf{k}'')}=\frac{v_{E(0)}(\mathbf{k}'\rho')\,v_{E(0)}(\mathbf{k}''\rho'')}{c^2} \tag{6.7c}$$

can be brought in front of the amplitudes (6.4). Hence, $W^s_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\rho'')$ is proportional to the energy transport velocities of both outgoing dressed polaritons and to a combination of anharmonic coupling constants, the coefficients of which are related to the exciton strength parameters introduced by Mills and Burstein [4]. They can be called generalized strength parameters, which include the exciton-phonon first-order interaction. The proportionality between $W^s_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\rho'')$ and the energy transport velocities is in agreement with the results of Mills and Burstein [4]. Their outgoing modes consist of a bare phonon and a bare polariton and, therefore, only $v_E(\mathbf{k}\rho)$ for the polariton mode appears in their results. It should be mentioned that far from the absorption region:

$$v_{p(0)}(\mathbf{k}\rho)=v_{E(0)}(\mathbf{k}\rho)=c\eta_0^{-1}(\mathbf{k}\rho)$$

and, hence, the amplitude (6.3) is also in general agreement with Ovander's results [19] for energies far from an absorption band and in the absence of spatial dispersion.

The total amplitude (6.3) is a well-behaved function of the incoming and outgoing frequencies. There are two critical regions in the spectrum where its behaviour must be examined more closely, namely when either the incoming energy or an outgoing frequency approaches an excitonic level $\bar{E}_{\mathbf{k}\lambda}$ or a phonon energy $\bar{\omega}_{\mathbf{k}\xi}$. No divergence appears in (6.3) in these two regions of the spectrum, contrary to the contentions of Loudon [2] and Birman and Ganguly [3]. They correspond to the resonance conditions of the Raman effect studied by many experimental [1] and theoretical [3], [4], [12] [14] workers. It can be seen that all the 'resonating' terms are contained in the coefficients (6.6) of the canonical transformation which have extremum values zero and unity. We will examine therefore the behaviour of these coefficients.

We consider first the specific case when the energy $\omega_{\rho(0)}(\mathbf{k})$ of the dressed polariton $(\mathbf{k}\rho)$ is in the vicinity of the excitonic level $\bar{E}_{\mathbf{k}\lambda}$. The screening factor can be approximated by

$$\lambda_0(\mathbf{k}\rho)\approx\frac{(\bar{E}_{\mathbf{k}\lambda}+\Delta_{\mathbf{k}\lambda})^2}{ck\bar{E}_{\mathbf{k}\lambda}\sum_{\epsilon}|\bar{f}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2}[\bar{E}_{\mathbf{k}\lambda}+\Delta_{\mathbf{k}\lambda}-\omega_{\rho(0)}(\mathbf{k})]^2\to 0 \tag{6.8a}$$

where $\Delta_{\mathbf{k}\lambda}=\sum_{\xi}2\omega_{\mathbf{k}\xi}|\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2/(\omega^2_{\rho(0)}(\mathbf{k})-\bar{\omega}^2_{\mathbf{k}\xi})$ is the energy shift arising from the exciton-lattice coupling H^1_{eL} already mentioned in Section IV. Using the limit (6.8a) and taking the proper limit in (6.6), we find that

$$u^{(0)}_{\epsilon\rho}(\mathbf{k})+v^{(0)}_{\epsilon\rho}(\mathbf{k})|\to 0 \qquad \text{and} \qquad |v^{(0)}_{\lambda\rho}(\mathbf{k})|\to 0,$$

while

$$|u^{(0)}_{\lambda\rho}(\mathbf{k})|\to 1 \qquad \text{and} \qquad |u^{(0)}_{\xi\rho}(\mathbf{k})+v^{(0)}_{\xi\rho}(\mathbf{k})|\to[4\omega^2_{\mathbf{k}\xi}|\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2]^{\frac{1}{2}}.$$

Thus, as $\omega_{\rho(0)}(\mathbf{k})\to\bar{E}_{\mathbf{k}\lambda}+\Delta_{\mathbf{k}\lambda}$, the photon content of the dressed polariton is decreasing while the $(\mathbf{k}\rho)$ mode becomes increasingly exciton-like with a small phonon part. At exact resonance conditions, the $(\mathbf{k}\rho)$ mode consists only of the $(\mathbf{k}\lambda)$ exciton with a slight phonon admixture, as if the photon field had been decoupled and will be called dressed exciton. The energy shift is seen to be directly proportional to the exciton-phonon coupling fnnction.

Consider now the case when $\omega_{\rho(0)}(\mathbf{k})$ is in the neighbourhood of the phonon energy $\bar{\omega}_{\mathbf{k}\xi}$. Retaining the leading term again, the screening factor can be approximated by

$$\lambda_0(\mathbf{k}\rho) = -\frac{(\bar{\omega}_{\mathbf{k}\xi}+\delta_{\mathbf{k}\xi})^2}{2ck\bar{\omega}_{\mathbf{k}\xi}\delta_{\mathbf{k}\xi}\alpha_0(\mathbf{k}\rho)}[\bar{\omega}_{\mathbf{k}\xi}+\delta_{\mathbf{k}\xi}-\omega_{\rho(0)}(\mathbf{k})]^2 \rightarrow \tag{6.8b}$$

where

$$\delta_{\mathbf{k}\xi} = -(\omega_{\mathbf{k}\xi}/\bar{\omega}_{\mathbf{k}\xi}) \sum_{\lambda} \bar{E}_{\mathbf{k}\lambda}|\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2/(\bar{E}^2_{\mathbf{k}\lambda}-\omega^2_{\rho(0)}(\mathbf{k}))$$

is the temperature dependent shift arising in the low energy part of the spectrum from H^1_{eL}. Using (6.8b) and taking again the proper limit in (6.6), we find that

$$|u^{(0)}_{\epsilon\rho}(\mathbf{k})+v^{(0)}_{\epsilon\rho}(\mathbf{k})| \rightarrow 0 \qquad \text{and} \qquad |u^{(0)}_{\xi\rho}(\mathbf{k})+v^{(0)}_{\epsilon\rho}(\mathbf{k})| \rightarrow (\omega_{\mathbf{k}\xi}/\bar{\omega}_{\mathbf{k}\xi}) \approx 1,$$

while the exciton coefficients remain finite, though small. Then, for $\omega_{\rho(0)}(\mathbf{k}) \rightarrow \bar{\omega}_{\mathbf{k}\xi}+\delta_{\mathbf{k}\xi}$, the photon content of the dressed polariton $(\mathbf{k}\rho)$ is decreasing, while its phonon content increases. At resonance, the $(\mathbf{k}\rho)$ mode is a dressed phonon made of the $(\mathbf{k}\xi)$ phonon with a slight exciton admixture, but without photon contribution, like in the case of the exciton resonance.

Hence no divergence occurs in either resonance conditions. It is easy now to see how the scattering amplitudes behave in a case of outgoing or incoming mode resonance. Let us suppose that the incoming energy $\omega_{\rho(0)}(\mathbf{k})$ is in the vicinity of the exciton level $\bar{E}_{\mathbf{k}\lambda}$. Then the scattering amplitude (6.3) is reduced to

$$\begin{aligned} W^s_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\rho'') = (\bar{E}_{\mathbf{k}\lambda}+\Delta_{\mathbf{k}\lambda})[1+n_{\rho'}(\mathbf{k}')+n_{\rho''}(\mathbf{k}'')][R_{\mathbf{k}\lambda}(\mathbf{k}'\rho',\mathbf{k}''\rho'') \\ + |u^{(0)}_{\xi\rho}(\mathbf{k})+v^{(0)}_{\xi\rho}(\mathbf{k})|^2 R_{\mathbf{k}\xi}(\mathbf{k}'\rho',\mathbf{k}''\rho'')]\,\delta_{\mathbf{k}'-\mathbf{k}'',\mathbf{k}}\delta(\bar{E}_{\mathbf{k}\lambda}+\Delta_{\mathbf{k}\lambda} \\ - \omega_{\rho'(0)}(\mathbf{k}')-\omega_{\rho''(0)}(\mathbf{k}'')), \end{aligned} \tag{6.9}$$

which describes the probability for the process where a dressed exciton decays into two dressed polaritons. The last term in (6.9) is the phonon scattering amplitude (6.4b), which is proportional to the exciton-phonon coupling constant and is, therefore, very small. If we further assume that at the same time there is a lattice resonance for one of the outgoing modes, i.e. $\omega_{\rho'(0)}(\mathbf{k}') \rightarrow \bar{\omega}_{\mathbf{k}'\xi'}+\delta_{\mathbf{k}'\xi'}$, then the total scattering amplitude $W^s_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\rho'')$ is given again by (6.9), but the expressions for $R_{\mathbf{k}\lambda}(\mathbf{k}'\rho',\mathbf{k}''\rho'')$ and $R_{\mathbf{k}\lambda}(\mathbf{k}'\rho',\mathbf{k}''\rho'')$ become

$$\begin{aligned} R_{\mathbf{k}\lambda}(\mathbf{k}'\rho',\mathbf{k}''\rho'') = \Big| \sum_{\lambda''} u^{(0)}_{\lambda''\rho''}(\mathbf{k}'')\,G_{\mathbf{k}'\xi'}(\mathbf{k}\lambda,\mathbf{k}''\lambda'') + \sum_{\lambda'\xi''} u^{(0)}_{\lambda'\rho'}(\mathbf{k}') \times [u^{(0)}_{\xi''\rho''}(\mathbf{k}'') \\ + v^{(0)}_{\xi''\rho''}(\mathbf{k}'')]\,G_{\mathbf{k}''\xi''}(\mathbf{k}\lambda,\mathbf{k}'\lambda') + \sum_{\lambda'\epsilon''} u^{(0)}_{\lambda'\rho'}(\mathbf{k}')[u^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')+v^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')] \\ \times [F_{\mathbf{k}''\epsilon''}(\mathbf{k}\lambda,\mathbf{k}'\lambda')+F^*_{\mathbf{k}''\epsilon''}(\mathbf{k}'\lambda',\mathbf{k}\lambda)] + \sum_{\xi''}[u^{(0)}_{\xi''\rho''}(\mathbf{k}'')+v^{(0)}_{\xi''\rho''}(\mathbf{k}'')] \\ \times [d_{\mathbf{k}'\xi'\mathbf{k}''\xi''}(\mathbf{k}\lambda)+d_{\mathbf{k}''\xi''\mathbf{k}'\xi'}(\mathbf{k}\lambda)] + \sum_{\epsilon''}[u^{(0)}_{\epsilon''\rho''}(\mathbf{k}'') \\ + v^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')]\,\theta_{\mathbf{k}'\xi'}(\mathbf{k}\lambda,\mathbf{k}''\epsilon'')\Big|^2, \end{aligned} \tag{6.10a}$$

$$R_{\mathbf{k}\xi}(\mathbf{k}'\rho',\mathbf{k}''\rho'') = \Big|\sum_{\lambda'\lambda''}[u^{(0)}_{\lambda'\rho'}(\mathbf{k}')\,v^{(0)}_{\lambda''\rho''}(\mathbf{k}'') + u^{(0)}_{\lambda''\rho''}(\mathbf{k}'')\,v^{(0)}_{\lambda'\rho'}(\mathbf{k}')] \times [G_{-\mathbf{k}\xi}(\mathbf{k}'\lambda',\mathbf{k}''\lambda'') + G^{*}_{-\mathbf{k}\xi}(\mathbf{k}''\lambda'',\mathbf{k}'\lambda')]\Big|^2 + \Big|\sum_{\lambda''}[u^{(0)}_{\lambda''\rho''}(\mathbf{k}'') - v^{(0)}_{\lambda''\rho''}(\mathbf{k}'')] \times [d_{\mathbf{k}'\xi'-\mathbf{k}\xi}(\mathbf{k}''\lambda'') + d_{-\mathbf{k}\xi\mathbf{k}'\xi'}(\mathbf{k}''\lambda'')] + \sum_{\lambda'\xi''}[u^{(0)}_{\lambda'\rho'}(\mathbf{k}') - v^{(0)}_{\lambda'\rho'}(\mathbf{k}')] \times [u^{(0)}_{\xi''\rho''}(\mathbf{k}'') + v^{(0)}_{\xi''\rho''}(\mathbf{k}'')][d_{\mathbf{k}''\xi''-\mathbf{k}\xi}(\mathbf{k}'\lambda') + d_{-\mathbf{k}\xi\mathbf{k}''\xi''}(\mathbf{k}'\lambda')] + \sum_{\lambda'\epsilon''}[u^{(0)}_{\lambda'\rho'}(\mathbf{k}') - v^{(0)}_{\lambda'\rho'}(\mathbf{k}')][u^{(0)}_{\epsilon''\rho''}(\mathbf{k}') + v^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')]\,\theta_{-\mathbf{k}\xi}(\mathbf{k}'\lambda',\mathbf{k}''\epsilon'')\Big|^2. \tag{6.10b}$$

(6.10a) and (6.10b) describe the probability for the decay of a dressed exciton into the dressed phonon $(\mathbf{k}'\rho')$ and the dressed polariton $(\mathbf{k}''\rho'')$.

The scattering amplitude (6.9), describing the incoming mode exciton resonance, consists of less terms than the full expression (6.3) which is valid far from resonance, but it also contains different screening factors. The magnitude of the resonance scattering probability (6.9) relative to (6.3) has to be computed for an actual crystal, in order to determine if there is a resonance enhancement or not at the energy $\bar{E}_{\mathbf{k}\lambda} + \Delta_{\mathbf{k}\lambda}$ higher than that of the free exciton. Similarly, when the outgoing $(\mathbf{k}'\rho')$ mode is in a lattice resonance condition, the partial probabilities (6.10) are made of less terms than the corresponding functions of (6.4), but, on the other hand, the screening factors represented by $u^{(0)}_{j\rho}(\mathbf{k})$ and $v^{(0)}_{j\rho}(\mathbf{k})$ are quite different in magnitude. Therefore, quantitative conclusions for the magnitude of the scattering probability (6.9) with and without outgoing resonance can be derived only by computation for a real crystal.

The amplitudes (6.3) describe the first-order Stokes scattering process of dressed polaritons. If the exciton-phonon coupling H^1_{eL} is weak, the dressing of the polariton by the phonon field is also weak, the energy shift $\Delta_{\mathbf{k}\lambda}$, and possibly $\delta_{\mathbf{k}\lambda}$, is small and can be neglected but not $\delta_{\mathbf{k}\xi}$. Also, the function $\Lambda_0(\mathbf{k}\rho)$ can be neglected in comparison to unity in the denominators of (6.6) but not in the numerators. This corresponds to neglecting most of the quantitative effects of H^1_{eL}, while retaining the qualitative consequence of dressing the polaritons. If we now consider that there is no exciton-lattice coupling, i.e., taking in (6.6) the limit $|\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2 = 0$ or using the results of the limiting case b), we obtain the (bare) polariton scattering probability

$$W^{s(u)}_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\rho'') + W^{s(u)}_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\xi'') + W^{s(u)}_{\mathbf{k}\rho}(\mathbf{k}'\xi',\mathbf{k}''\xi'') = \omega^{(u)}_{\rho(0)}(\mathbf{k})\,\bar{\lambda}_0^{-1}(\mathbf{k}\rho) \times \{(1 + n_{\rho'}(\mathbf{k}') + n_{\rho''}(\mathbf{k}''))[|u^{(0)u}_{\epsilon\rho}(\mathbf{k}) + v^{(0)u}_{\epsilon\rho}(\mathbf{k})|^2 R^u_{\mathbf{k}\epsilon}(\mathbf{k}'\rho',\mathbf{k}''\rho'') + |u^{(0)u}_{\lambda\rho}(\mathbf{k}) - v^{(0)u}_{\lambda\rho}(\mathbf{k})|^2 \times R^u_{\mathbf{k}\lambda}(\mathbf{k}'\rho',\mathbf{k}''\rho'')]\,\delta(\omega^{(u)}_{\rho(0)}(\mathbf{k}) - \omega^{(u)}_{\rho'(0)}(\mathbf{k}') - \omega^{(u)}_{\rho''(0)}(\mathbf{k}'')) + [1 + n_{\rho'}(\mathbf{k}') + N_{\xi''}(\mathbf{k}'')] \times [|u^{(0)u}_{\epsilon\rho}(\mathbf{k}) + v^{(0)u}_{\epsilon\rho}(\mathbf{k})|^2 R^u_{\mathbf{k}\epsilon}(\mathbf{k}'\rho',\mathbf{k}''\xi'') + |u^{(0)u}_{\lambda\rho}(\mathbf{k}) - v^{(0)u}_{\lambda\rho}(\mathbf{k})|^2 R^u_{\mathbf{k}\lambda}(\mathbf{k}'\rho',\mathbf{k}''\xi'')] \times \delta(\omega^{(u)}_{\rho(0)}(\mathbf{k}) - \omega^{(u)}_{\rho'(0)}(\mathbf{k}') - \bar{\omega}_{\mathbf{k}''\xi''}) + [1 + N_{\xi'}(\mathbf{k}') + N_{\xi''}(\mathbf{k}'')]|u^{(0)u}_{\lambda\rho}(\mathbf{k}) - v^{(0)u}_{\lambda\rho}(\mathbf{k})|^2 \times R^u_{\mathbf{k}\lambda}(\mathbf{k}'\xi',\mathbf{k}''\xi'')\,\delta(\omega^{(u)}_{\rho(0)}(\mathbf{k}) - \bar{\omega}_{\mathbf{k}'\xi'} - \bar{\omega}_{\mathbf{k}''\xi''})\}\,\delta_{\mathbf{k}'-\mathbf{k}'',\mathbf{k}}, \tag{6.11}$$

where

$$N_\xi(\mathbf{k}) = \langle b^\dagger_{\mathbf{k}\xi} b_{\mathbf{k}\xi}\rangle_{(0)}$$

$$\bar{\lambda}_0(\mathbf{k}\rho) = \lim_{|\tilde{g}_{\mathbf{k}\epsilon}(\mathbf{k}\lambda)|^2 = 0} \lambda_0(\mathbf{k}\rho), \tag{6.12}$$

and the partial scattering amplitudes are given by

$$R^u_{\mathbf{k}\epsilon}(\mathbf{k}'\rho', \mathbf{k}''\rho'') = \Big|\sum_{\lambda'\lambda''} [u^{(0)u}_{\lambda'\rho'}(\mathbf{k}')\, v^{(0)u}_{\lambda''\rho''}(\mathbf{k}'') + u^{(0)u}_{\lambda''\rho''}(\mathbf{k}'')\, v^{(0)u}_{\lambda'\rho'}(\mathbf{k}')] \times [F_{-\mathbf{k}\epsilon}(\mathbf{k}'\lambda', \mathbf{k}''\lambda'') + F^*_{-\mathbf{k}\epsilon}(\mathbf{k}''\lambda'', \mathbf{k}'\lambda')]\Big|^2, \tag{6.13}$$

$$R^u_{\mathbf{k}\lambda}(\mathbf{k}'\rho', \mathbf{k}''\rho'') = \Big|\sum_{\lambda'\epsilon''} u^{(0)u}_{\lambda'\rho'}(\mathbf{k}')[u^{(0)u}_{\epsilon''\rho''}(\mathbf{k}'') + v^{(0)u}_{\epsilon''\rho''}(\mathbf{k}'')] \times [F_{+\mathbf{k}''\epsilon''}(\mathbf{k}\lambda, \mathbf{k}'\lambda') + F^*_{\mathbf{k}''\epsilon''}(\mathbf{k}'\lambda', \mathbf{k}\lambda)] + \text{interch.}\Big|^2,$$

$$R^u_{\mathbf{k}\epsilon}(\mathbf{k}'\rho', \mathbf{k}''\xi'') = \Big|\sum_{\epsilon'} [u^{(0)u}_{\epsilon'\rho'}(\mathbf{k}') + v^{(0)u}_{\epsilon'\rho'}(\mathbf{k}')][\phi_{\mathbf{k}''\xi''}(\mathbf{k}'\epsilon', -\mathbf{k}\epsilon) + \phi_{\mathbf{k}''\xi''}(\mathbf{k}\epsilon, -\mathbf{k}'\epsilon')]\Big|^2 + \Big|\sum_{\lambda'} [u^{(0)u}_{\lambda'\rho'}(\mathbf{k}') - v^{(0)u}_{\lambda'\rho'}(\mathbf{k}')]\, \theta_{\mathbf{k}''\xi''}(\mathbf{k}'\lambda', -\mathbf{k}\epsilon)\Big|^2, \tag{6.14a}$$

$$R^u_{\mathbf{k}\lambda}(\mathbf{k}'\rho', \mathbf{k}''\xi'') = \Big|\sum_{\lambda'} u^{(0)u}_{\lambda'\rho'}(\mathbf{k}')\, G_{\mathbf{k}''\xi''}(\mathbf{k}\lambda, \mathbf{k}'\lambda') + \sum_{\epsilon'} [u^{(0)u}_{\epsilon'\rho'}(\mathbf{k}') + v^{(0)u}_{\epsilon'\rho'}(\mathbf{k}')]\, \theta_{\mathbf{k}''\xi''}(\mathbf{k}\lambda, \mathbf{k}'\lambda')\Big|^2, \tag{6.14b}$$

$$R^u_{\mathbf{k}\lambda}(\mathbf{k}'\xi', \mathbf{k}''\xi'') = |d_{\mathbf{k}'\xi'\mathbf{k}''\xi''}(\mathbf{k}\lambda) + d_{\mathbf{k}''\xi''\mathbf{k}'\xi'}(\mathbf{k}\lambda)|^2. \tag{6.15}$$

The coefficients $u^{(0)u}_{j\rho}(\mathbf{k})$ and $v^{(0)u}_{j\rho}(\mathbf{k})$ can be obtained from (6.6) after taking the limit $|\tilde{g}_{\mathbf{k}\xi}(\mathbf{k}\lambda)|^2 = 0$ and the bare polariton energy $\omega^{(u)}_{\rho(0)}(\mathbf{k})$ is determined by the roots of the secular equation (5.15).

The expression for the scattering amplitude (6.11) consists of three different terms. The first term on the right-hand side of (6.11), which corresponds to $W^{s(u)}_{\mathbf{k}\rho}(\mathbf{k}'\rho', \mathbf{k}''\rho'')$, describes the decay into two polaritons. Such polariton-polariton scattering takes place at the high energy region of the spectrum and arises from the H^2_{eeR} anharmonic part of the Hamiltonian. The last term in (6.11), which corresponds to $W^{s(u)}_{\mathbf{k}\rho}(\mathbf{k}'\xi', \mathbf{k}''\xi'')$, gives the probability for the decay of a polariton into phonons and arises from the H^2_{eLL} of the Hamiltonian (2.4a). The physical process in question takes place in the infrared region of the spectrum.

In the optical region of frequencies, the second term in (6.11) is predominant and describes the probability, $W^{s(u)}_{\mathbf{k}\rho}(\mathbf{k}'\rho', \mathbf{k}''\xi'')$, where the incoming polariton is scattered into a polariton and a phonon. This process corresponds to the Raman effect studied by Mills and Burstein [4]. The amplitude $W^{s(u)}_{\mathbf{k}\rho}(\mathbf{k}'\rho', \mathbf{k}''\xi'')$ consists of contributions arising from the exciton and photon scattering probabilities $R^u_{\mathbf{k}\lambda}(\mathbf{k}'\rho', \mathbf{k}''\xi'')$ and $R^u_{\mathbf{k}\epsilon}(\mathbf{k}'\rho', \mathbf{k}''\xi'')$ respectively, and is a function of the polariton and phonon occupation numbers. Since the polariton energy is much larger than the thermal energy $k_B T$ for normal temperatures, the polariton occupation number $n_{\rho'}(\mathbf{k}')$ can be discarded. Thus, the temperature dependence arises only from the phonon occupation number $N_{\xi''}(\mathbf{k}'')$. A weak temperature dependence may also arise through the expressions for the coefficients $u^{(0)u}_{j\rho}(\mathbf{k})$ and $v^{(0)u}_{j\rho}(\mathbf{k})$ and the arguments of the delta function. The amplitude $W^{s(u)}_{\mathbf{k}\rho}(\mathbf{k}'\rho', \mathbf{k}''\xi'')$ can be expressed as a function of the energy transport velocities of both incoming and outgoing polaritons and of a two polariton–one phonon effective coupling constant, which originates from the H^2_{RRL}, H^2_{eRL} and H^2_{eeL} terms of the Hamiltonian. The total amplitude, therefore, can be rewritten as

$$\begin{aligned} W^{s(u)}_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\xi'') &= \omega^{(u)}_{\rho(0)}(\mathbf{k})\,\bar{\lambda}_0^{-1}(\mathbf{k}\rho)[1+N_{\xi''}(\mathbf{k}'')]\,v^u_E(\mathbf{k}\rho)\,v^u_E(\mathbf{k}'\rho')/c^2 \\ &\times\Bigg[\Big|\sum_{\epsilon'}(\phi_{\mathbf{k}''\xi''}(\mathbf{k}'\epsilon',-\mathbf{k}\epsilon)+\phi_{\mathbf{k}''\xi''}(\mathbf{k}\epsilon,-\mathbf{k}'\epsilon'))\Big|^2 \\ &+\Big|\sum_{\lambda'}2\alpha_0^{\frac{1}{2}}(\mathbf{k}'\rho')[\bar{E}_{\mathbf{k}'\lambda'}/\bar{E}^2_{\mathbf{k}'\lambda'}-\omega^{(u)2}_{\rho'(0)}(\mathbf{k}')]^{\frac{1}{2}}\times\theta_{\mathbf{k}''\xi''}(\mathbf{k}'\lambda',-\mathbf{k}\epsilon\Big|^2 \\ &+2\alpha_0(\mathbf{k}\rho)[\bar{E}_{\mathbf{k}\lambda}/\bar{E}^2_{\mathbf{k}\lambda}-\omega^{(u)2}_{\rho(0)}(\mathbf{k})]\Big|\sum_{\epsilon'}\phi_{\mathbf{k}''\xi''}(\mathbf{k}\lambda,\mathbf{k}'\epsilon') \\ &+\sum_{\lambda'}\alpha_0^{\frac{1}{2}}(\mathbf{k}'\rho')[\bar{E}_{\mathbf{k}'\lambda'}/\bar{E}^2_{\mathbf{k}'\lambda'}-\omega^{(u)2}_{\rho'(0)}(\mathbf{k}')]^{\frac{1}{2}}[\bar{E}_{\mathbf{k}'\lambda'} \\ &+\omega^{(u)}_{\rho'(0)}(\mathbf{k}')]/\bar{E}_{\mathbf{k}'\lambda'}G_{\mathbf{k}''\xi''}(\mathbf{k}\lambda,\mathbf{k}'\lambda')\Big|^2\Bigg]\times\delta(\omega^{(u)}_{\rho(0)}(\mathbf{k})-\omega^{(u)}_{\rho'(0)}(\mathbf{k}') \\ &-\bar{\omega}_{\mathbf{k}''\xi''})\,\delta_{\mathbf{k}'-\mathbf{k}'',\mathbf{k}}, \end{aligned} \tag{6.16}$$

where the effective coupling constant is defined by the expressions in the square brackets. The expression (6.16) can be compared with the matrix element $\mathscr{M}_{11}$ of Mills and Burstein, which is in turn proportional to the Raman tensor introduced by Loudon [2]. Allowing for differences in notation, a connection can be established with the results of Reference [4] if we retain in (6.16) only the H^2_{eeL} interaction term with the corresponding coupling constant $G_{\mathbf{k}''\xi''}(\mathbf{k}\lambda,\mathbf{k}'\lambda')$ and discard all the remaining anharmonic interactions. Then, their $\mathscr{M}_{11}(\mathbf{q}_I\lambda_I,\mathbf{q}_s\lambda_s;\lambda_p)$ corresponds to

$$|u^{(0)u}_{\lambda_I\rho_I}(\mathbf{q}_I)|\cdot|u^{(0)u}_{\lambda_s\rho_s}(\mathbf{q}_s)|\cdot|G_{\mathbf{k}_p\lambda_p}(\mathbf{q}_I\lambda_I,\mathbf{q}_s\lambda_s)|^2.$$

Hence, $\mathscr{M}_{11}$ represents only one contribution of the polariton-phonon scattering amplitude (6.16). In the latter, the effective coupling function can be further simplified by assuming that cross products of different anharmonic coupling constants can be neglected. Hence, (6.16) becomes

$$\begin{aligned} W^{s(u)}_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\xi'') &= \omega^{(u)}_{\rho(0)}(\mathbf{k})\,\bar{\lambda}_0^{-1}(\mathbf{k}\rho)[1+N_{\xi''}(\mathbf{k}'')]\,v^u_E(\mathbf{k}\rho)\,v^u_E(\mathbf{k}'\rho')/c^2 \\ &\times\Bigg[\Big|\sum_{\epsilon'}(\phi_{\mathbf{k}''\xi''}(\mathbf{k}'\epsilon',-\mathbf{k}\epsilon)+\phi_{\mathbf{k}''\xi''}(\mathbf{k}\epsilon,-\mathbf{k}'\epsilon'))\Big|^2 \\ &+\Big|\sum_{\lambda'}2\alpha_0^{\frac{1}{2}}(\mathbf{k}'\rho')\left(\frac{\bar{E}_{\mathbf{k}'\lambda'}}{\bar{E}^2_{\mathbf{k}'\lambda'}-\omega^{(u)2}_{\rho'(0)}(\mathbf{k}')}\right)^{\frac{1}{2}}\times\theta_{\mathbf{k}''\xi''}(\mathbf{k}'\lambda',-\mathbf{k}\epsilon)\Big|^2 \\ &+2\alpha_0(\mathbf{k}\rho)\frac{\bar{E}_{\mathbf{k}\lambda}}{[\bar{E}^2_{\mathbf{k}\lambda}-\omega^{(u)2}_{\mathbf{k}(0)}(\mathbf{k})]}\Big|\sum_{\epsilon'}\theta_{\mathbf{k}''\xi''}(\mathbf{k}\lambda,\mathbf{k}'\epsilon')\Big|^2 \\ &+2\alpha_0(\mathbf{k}\rho)\frac{\bar{E}_{\mathbf{k}\lambda}}{[\bar{E}^2_{\mathbf{k}\lambda}-\omega^{(u)2}_{\rho(0)}(\mathbf{k})]}\Big|\sum_{\lambda'}\alpha_0^{\frac{1}{2}}(\mathbf{k}'\rho')\left(\frac{\bar{E}_{\mathbf{k}'\lambda'}}{\bar{E}^2_{\mathbf{k}'\lambda'}-\omega^{(u)2}_{\rho'(0)}(\mathbf{k}')}\right)^{\frac{1}{2}} \\ &\times\frac{\bar{E}_{\mathbf{k}'\lambda'}+\omega^{(u)}_{\rho'(0)}(\mathbf{k}')]}{\bar{E}_{\mathbf{k}'\lambda'}}\times G_{\mathbf{k}''\xi''}(\mathbf{k}\lambda,\mathbf{k}'\lambda')\Big|^2\Bigg]\delta(\omega^{(u)}_{\rho(0)}(\mathbf{k})-\omega^{(u)}_{\rho'(0)}(\mathbf{k}') \\ &-\bar{\omega}_{\mathbf{k}''\xi''})\,\delta_{\mathbf{k}'-\mathbf{k}''-\mathbf{k}}. \end{aligned} \tag{6.17}$$

The first term in the expression (6.17) arises from the anharmonic Hamiltonian H^2_{RRL}, which describes photon-photon scattering through the emission of a phonon. This term is present even in the absence of dispersion since it is caused by the anharmonic part of the electromagnetic field. The second and third terms in (6.17) originate from H^2_{eRL} and describe exciton-photon scattering processes with the emission of a phonon and vanish in the absence of dispersion. The fourth term comes from the anharmonic Hamiltonian H^2_{eeL} and represents the process, where an exciton is scattered into another exciton and a phonon. Retaining only the largest terms having small energy denominators in

$$\alpha_0(\mathbf{k}\rho)\,\frac{\bar{E}_{\mathbf{k}\lambda}}{[\bar{E}^2_{\mathbf{k}'\lambda}-\omega^{(u)2}_{\rho(0)}(\mathbf{k})]}$$

for both incoming and outgoing modes and ignoring the energy mode transport velocities, we recover the perturbation theoretical results of Loudon [2] and Birman and Ganguly [3], which are valid approximately far from resonance regions.

Resonance conditions can be met in the excitonic part of the spectrum only by both oncoming and outgoing polaritons. If the incoming energy $\omega^u_{\rho(0)}(\mathbf{k})$ is in the vicinity of the $\bar{E}_{\mathbf{k}\lambda}$ exciton level, the probability (6.16) reduces to

$$\begin{aligned} W^{s(u)}_{\mathbf{k}\lambda}(\mathbf{k}'\rho',\mathbf{k}''\xi'') = \bar{E}_{\mathbf{k}\lambda}[1+N_{\xi''}(\mathbf{k}'')]\,v^u_E(\mathbf{k}'\rho')/c^2\Bigg[\Bigg|\sum_{\epsilon'}\theta_{\mathbf{k}''\xi''}(\mathbf{k}\lambda,\mathbf{k}'\epsilon') \\ + \sum_{\lambda'}\alpha_0^{\frac{1}{2}}(\mathbf{k}'\rho')\left(\frac{\bar{E}_{\mathbf{k}'\lambda'}}{\bar{E}^2_{\mathbf{k}'\lambda'}-\omega^{u2}_{\rho'(0)}(\mathbf{k}')}\right)^{\frac{1}{2}}\frac{[\bar{E}_{\mathbf{k}'\lambda'}+\omega^u_{\rho'(0)}(\mathbf{k}')]}{\bar{E}_{\mathbf{k}'\lambda'}} \\ \times G_{\mathbf{k}''\xi''}(\mathbf{k}\lambda,\mathbf{k}'\lambda')\Bigg|^2\Bigg]\times\delta(\bar{E}_{\mathbf{k}\lambda}-\omega^u_{\rho'(0)}(\mathbf{k}')-\bar{\omega}_{\mathbf{k}''\xi''})\,\delta_{\mathbf{k}'-\mathbf{k}'',\mathbf{k}}, \end{aligned} \tag{6.18a}$$

indicating that the bare $(\mathbf{k}\lambda)$ exciton mode decays into the $(\mathbf{k}''\xi'')$ phonon and the $(\mathbf{k}'\rho')$ polariton. On the other hand, if the outgoing mode has an energy $\omega^u_{\rho'(0)}(\mathbf{k}')$ close to the excitonic $(\mathbf{k}'\lambda')$ level, the expression (6.16) becomes

$$\begin{aligned} W^{s(u)}_{\mathbf{k}\rho}(\mathbf{k}'\lambda',\mathbf{k}''\xi'') = \omega^u_{\rho(0)}(\mathbf{k})[1+N_{\xi''}(\mathbf{k}'')]\,v^u_E(\mathbf{k}\rho)/c\Bigg[|\theta_{\mathbf{k}''\xi''}(\mathbf{k}'\lambda',-\mathbf{k}\epsilon)|^2 \\ + 2\alpha_0(\mathbf{k}\rho)\,\frac{\bar{E}_{\mathbf{k}\lambda}}{[\bar{E}^2_{\mathbf{k}\lambda}-\omega^{u2}_{\rho(0)}(\mathbf{k})]}\,|G_{\mathbf{k}''\xi''}(\mathbf{k}\lambda,\mathbf{k}'\lambda')|^2\Bigg]\,\delta(\omega^u_{\rho(0)}(\mathbf{k}) \\ -\bar{E}_{\mathbf{k}'\lambda'}-\bar{\omega}_{\mathbf{k}''\xi''})\,\delta_{\mathbf{k}'-\mathbf{k}'',\mathbf{k}}, \end{aligned} \tag{6.18b}$$

and describes the decay of $(\mathbf{k}\rho)$ mode into the $(\mathbf{k}'\lambda')$ exciton and the $(\mathbf{k}''\xi'')$ phonon.

The relative importance of the expression (6.18) and (6.16) or (6.17) can be found only by their computation for real crystals. The existence of resonance enhancement in the scattering amplitude is difficult to ascertain analytically, since some contributions to $W^{s(u)}_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\xi'')$ vanish in the resonance regime, whereas the screening coefficients $u^{(0)u}_{j\rho}(\mathbf{k})$ and $v^{(0)u}_{j\rho}(\mathbf{k})$ reach extremum values.

The specific case, where the three fields are independent of one another, is described by the Green functions (3.25). The photon life time is given by the function $\mathrm{Im}P_{22}(\mathbf{k}\omega)$, from which we derive the following scattering amplitudes.

$$
\begin{aligned}
W^{s}_{\mathbf{k}\epsilon}(\mathbf{k}'\lambda',\mathbf{k}''\xi'') + W^{s}_{\mathbf{k}\epsilon}(\mathbf{k}'\epsilon',\mathbf{k}''\xi'') &= 2ck[1 + N_{\lambda'}(\mathbf{k}') + N_{\xi''}(\mathbf{k}'')]|\theta_{\mathbf{k}''\xi''}(\mathbf{k}'\lambda',-\mathbf{k}\epsilon)|^2 \\
&\times \delta_{\mathbf{k}'-\mathbf{k}'',\mathbf{k}}\delta(\omega - \bar{E}_{\mathbf{k}'\lambda'} - \bar{\omega}_{\mathbf{k}''\xi''}) + 2ck[1 + N_{\epsilon'}(\mathbf{k}') \\
&+ N_{\xi''}(\mathbf{k}'')]|\phi_{\mathbf{k}''\xi''}(\mathbf{k}'\epsilon',-\mathbf{k}\epsilon) + \phi_{\mathbf{k}''\xi''}(\mathbf{k}\epsilon,-\mathbf{k}'\epsilon')|^2 \\
&\times \delta_{\mathbf{k}'-\mathbf{k}'',\mathbf{k}}\delta(\omega - (c^2k'^2 + \omega_p^2)^{\frac{1}{2}} - \bar{\omega}_{\mathbf{k}''\xi''}),
\end{aligned} \tag{6.19}
$$

where both the exciton $N_\lambda(\mathbf{k}) = \langle \alpha^\dagger_{\mathbf{k}\lambda}\alpha_{\mathbf{k}\lambda}\rangle_{(0)}$ and the photon $N_\epsilon(\mathbf{k}) = \langle A^\dagger_{\mathbf{k}\epsilon}A_{\mathbf{k}\epsilon}\rangle_{(0)}$ occupation numbers can be neglected. The first term in (6.19) gives the probability for the process where an exciton and a phonon are created through the absorption of a photon. The H^2_{eRL} part of the Hamiltonian is responsible for the process in question, which does not contribute to the first-order Raman effect. The second term in (6.19) is the probability of direct Raman effect, where the incoming photon is scattered into a photon and a phonon. Hence, the H^2_{RRL} part of the Hamiltonian is the only anharmonic interaction (for our model), which contributes to the Stokes component of first-order Raman scattering, in the absence of dispersion. Furthermore, no resonance occurs in the frequency dependence of the scattering amplitude.

b) Second-order scattering

We will now briefly examine the second-order Raman effect retaining only the Stokes component. The scattering amplitude is given by

$$
\begin{aligned}
W^{s}_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\rho'',\mathbf{k}'''\rho''') &= \omega_{\rho(0)}(\mathbf{k})\,\lambda_0^{-1}(\mathbf{k}\rho)[|u^{(0)}_{\epsilon\rho}(\mathbf{k}) + v^{(0)}_{\epsilon\rho}(\mathbf{k})|^2 R_{\mathbf{k}\epsilon}(\mathbf{k}'\rho',\mathbf{k}''\rho'',\mathbf{k}'''\rho''') \\
&+ |u^{(0)}_{\xi\rho}(\mathbf{k}) + v^{(0)}_{\xi\rho}(\mathbf{k})|^2 R_{\mathbf{k}\xi}(\mathbf{k}'\rho',\mathbf{k}''\rho'',\mathbf{k}'''\rho''') + |u^{(0)}_{\lambda\rho}(\mathbf{k}) \\
&- v^{(0)}_{\lambda\rho}(\mathbf{k})|^2 R_{\mathbf{k}\lambda}(\mathbf{k}'\rho',\ \mathbf{k}''\rho'',\ \mathbf{k}'''\rho''')] \times [1 + n_{\rho'}(\mathbf{k}') + n_{\rho''}(\mathbf{k}'') \\
&+ n_{\rho'''}(\mathbf{k}''') + n_{\rho'}(\mathbf{k}')\,n_{\rho''}(\mathbf{k}'') + n_{\rho''}(\mathbf{k}'')\,n_{\rho'''}(\mathbf{k}''') \\
&+ n_{\rho'''}(\mathbf{k}''')\,n_{\rho'}(\mathbf{k}')]\,\delta_{\mathbf{k}'-\mathbf{k}''-\mathbf{k}''',\mathbf{k}} \times \delta(\omega_{\rho(0)}(\mathbf{k}) - \omega_{\rho'(0)}(\mathbf{k}') \\
&- \omega_{\rho''(0)}(\mathbf{k}'') - \omega_{\rho'''(0)}(\mathbf{k}''')),
\end{aligned} \tag{6.20}
$$

where the partial probabilities are defined as

$$
\begin{aligned}
R_{\mathbf{k}\epsilon}(\mathbf{k}'\rho',\mathbf{k}''\rho'',\mathbf{k}'''\rho''') = \tfrac{1}{6}\Bigg| &\sum_{\substack{\lambda'\lambda''\lambda''' \\ \xi'\xi''\xi'''}} [u^{(0)}_{\lambda'\rho'}(\mathbf{k}') - v^{(0)}_{\lambda'\rho'}(\mathbf{k}')]\cdot[u^{(0)}_{\xi''\rho''}(\mathbf{k}'') + v^{(0)}_{\xi''\rho''}(\mathbf{k}'')] \times [u^{(0)}_{\xi'''\rho'''}(\mathbf{k}''') \\
&+ v^{(0)}_{\xi'''\rho'''}(\mathbf{k}''')]\cdot[\theta_{\mathbf{k}''\xi''\mathbf{k}'''\xi'''}(\mathbf{k}'\lambda',\mathbf{k}\epsilon) + \theta_{\mathbf{k}'''\xi'''\mathbf{k}''\xi''}(\mathbf{k}'\lambda',\mathbf{k}\epsilon)] \\
&+ \text{interch.}]\Bigg|^2,
\end{aligned} \tag{6.21a}
$$

$$
\begin{aligned}
R_{\mathbf{k}\lambda}(\mathbf{k}'\rho',\mathbf{k}''\rho'',\mathbf{k}'''\rho''') = \tfrac{1}{6}\Bigg| &\sum_{\substack{\lambda'\lambda''\lambda''' \\ \xi'\xi''\xi'''}} [(u^{(0)}_{\lambda'\rho'}(\mathbf{k}'))\cdot[u^{(0)}_{\xi''\rho''}(\mathbf{k}''') + v^{(0)}_{\xi''\rho''}(\mathbf{k}'')] \times [u^{(0)}_{\xi'''\rho'''}(\mathbf{k}''') \\
&+ v^{(0)}_{\xi'''\rho'''}(\mathbf{k}''')]\,D_{\mathbf{k}''\xi''\mathbf{k}'''\xi'''}(\mathbf{k}\lambda,\mathbf{k}'\lambda') + \text{interch.}] + \sum_{\substack{\epsilon'\epsilon''\epsilon''' \\ \xi'\xi''\xi'''}} [[u^{(0)}_{\epsilon'\rho'}(\mathbf{k}') \\
&+ v^{(0)}_{\epsilon'\rho'}(\mathbf{k}')] \times [u^{(0)}_{\xi''\rho''}(\mathbf{k}'') + v^{(0)}_{\xi''\rho''}(\mathbf{k}'')]\cdot[u^{(0)}_{\xi'''\rho'''}(\mathbf{k}''') \\
&+ v^{(0)}_{\xi'''\rho'''}(\mathbf{k}''')]\,\theta_{-\mathbf{k}''\xi''-\mathbf{k}'''\xi'''}(\mathbf{k}\lambda,\mathbf{k}'\epsilon') + \text{interch.}]\Bigg|^2,
\end{aligned} \tag{6.21b}
$$

$$R_{\mathbf{k}\xi}(\mathbf{k}'\rho',\mathbf{k}''\rho'',\mathbf{k}'''\rho''') = \tfrac{1}{6}\Bigg|\sum_{\substack{\lambda'\lambda''\lambda'''\\ \epsilon'\epsilon''\epsilon'''\\ \xi'\xi''\xi'''}} [u^{(0)}_{\lambda'\rho'}(\mathbf{k}') - v^{(0)}_{\lambda'\rho'}(\mathbf{k}')]\cdot[u^{(0)}_{\epsilon''\rho''}(\mathbf{k}'') + v^{(0)}_{\epsilon''\rho''}(\mathbf{k}'')]\times[u^{(0)}_{\xi'''\rho'''}(\mathbf{k}''') + v^{(0)}_{\xi'''\rho'''}(\mathbf{k}''')]\,\theta_{\mathbf{k}'''\xi'''\mathbf{k}\xi}(\mathbf{k}'\lambda',\mathbf{k}''\epsilon'') + \text{interch.}\Bigg|^2$$
$$+ \tfrac{2}{3}\Bigg|\sum_{\substack{\lambda'\lambda''\lambda'''\\ \xi'\xi''\xi'''}} [u^{(0)}_{\lambda'\rho'}(\mathbf{k}')\,v^{(0)}_{\lambda''\rho''}(\mathbf{k}'') + u^{(0)}_{\lambda''\rho''}(\mathbf{k}'')\,v^{(0)}_{\lambda'\rho'}(\mathbf{k}')]\cdot[u^{(0)}_{\xi'''\rho'''}(\mathbf{k}''') + v^{(0)}_{\xi'''\rho'''}(\mathbf{k}''')]\,D_{-\mathbf{k}'''\xi'''\mathbf{k}\xi}(\mathbf{k}'\lambda',\mathbf{k}''\lambda'') + \text{interch.}\Bigg|^2. \tag{6.21c}$$

In the dressed polariton representation, the second-order scattering amplitude (6.20) is fully symmetric with respect to the permutation of the indices of the outgoing modes. Like the first-order probability, (6.20) is a linear combination of partial probabilities, the coefficients of which are the $u^{(0)}_{j\rho}(\mathbf{k})$'s and $v^{(0)}_{j\rho}(\mathbf{k})$'s of the canonical transformation. These partial probabilities (6.21) are also polariton-like combinations of the coupling functions arising from the quartic anharmonicity H^3. Inspection of the expression (6.20) indicates that the resonant behaviour of $W^s_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\rho'',\mathbf{k}'''\rho''')$ is similar to that of the first-order probability and we will not discuss it any further. We only emphasize that in the dressed polariton representation there are two resonance regions, namely in the excitonic part of the spectrum and in the phonon region, where the energy shifts must be taken into account.

If we assume that the exciton-lattice coupling vanishes, then the amplitude (6.20) is reduced to

$$W^{s(u)}_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\xi'',\mathbf{k}'''\xi''') = \omega^{(u)}_{\rho(0)}((\mathbf{k})\,\bar{\lambda}_0^{-1}(\mathbf{k}\rho)[|u^{(0)u}_{\epsilon\rho}(\mathbf{k}) + v^{(0)u}_{\epsilon\rho}(\mathbf{k})|^2\,R^u_{\mathbf{k}\epsilon}(\mathbf{k}'\rho',\mathbf{k}''\xi'',\mathbf{k}'''\xi''')$$
$$+ |u^{(0)u}_{\lambda\rho}(\mathbf{k}) - v^{(0)u}_{\lambda\rho}(\mathbf{k})|^2\,R^u_{\mathbf{k}\lambda}(\mathbf{k}'\rho',\mathbf{k}''\xi'',\mathbf{k}'''\xi''')][1 + N_{\xi''}(\mathbf{k}'')$$
$$+ N_{\xi'''}(\mathbf{k}''') + N_{\xi''}(\mathbf{k}'')\,N_{\xi'''}(\mathbf{k}'')] \times \delta(\omega^{(u)}_{\rho(0)}(\mathbf{k}) - \omega^{(u)}_{\rho'(0)}(\mathbf{k}')$$
$$- \bar{\omega}_{\mathbf{k}''\xi''} - \bar{\omega}_{\mathbf{k}'''\xi'''})\,\delta_{\mathbf{k}'-\mathbf{k}''-\mathbf{k}''',\mathbf{k}}, \tag{6.22}$$

with the definitions:

$$R^u_{\mathbf{k}\epsilon}(\mathbf{k}'\rho',\mathbf{k}''\xi'',\mathbf{k}'''\xi''') = \tfrac{1}{2}\Bigg|\sum_{\lambda'} [u^{(0)u}_{\lambda'\rho'}(\mathbf{k}') - v^{(0)u}_{\lambda'\rho'}(\mathbf{k}')][\theta_{\mathbf{k}''\xi''\mathbf{k}'''\xi'''}(\mathbf{k}'\lambda',\mathbf{k}\epsilon) + \theta_{\mathbf{k}'''\xi'''\mathbf{k}''\xi''}(\mathbf{k}'\lambda',\mathbf{k}\epsilon)]\Bigg|^2, \tag{6.23}$$

$$R^u_{\mathbf{k}\lambda}(\mathbf{k}'\rho',\mathbf{k}''\xi'',\mathbf{k}'''\xi''') = \tfrac{1}{2}\Bigg|\sum_{\lambda'} u^{(0)u}_{\lambda'\rho'}(\mathbf{k}')[D_{\mathbf{k}''\xi''\mathbf{k}'''\xi'''}(\mathbf{k}\lambda,\mathbf{k}'\lambda') + D_{\mathbf{k}'''\xi'''\mathbf{k}''\xi''}(\mathbf{k}\lambda,\mathbf{k}'\lambda')]$$
$$+ \sum_{\epsilon'} [u^{(0)u}_{\epsilon'\rho'}(\mathbf{k}') + v^{(0)u}_{\epsilon'\rho'}(\mathbf{k}')][\theta_{-\mathbf{k}''\xi''-\mathbf{k}'''\xi'''}(\mathbf{k}\lambda,\mathbf{k}'\epsilon') + \theta_{-\mathbf{k}'''\xi'''-\mathbf{k}''\xi''}(\mathbf{k}\lambda,\mathbf{k}'\lambda')]\Bigg|^2.$$

In (6.22), the polariton occupation number $n_\rho(\mathbf{k})$ has been discarded. It can be seen from $W^{s(u)}_{\mathbf{k}\rho}(\mathbf{k}'\rho',\mathbf{k}''\xi'',\mathbf{k}'''\xi''')$ that our quartic anharmonicity leads, in the bare polariton representation, to the scattering of the incoming polariton into another polariton and two phonons. Furthermore, the bare photon scattering amplitude obtained from $R^{u}_{\mathbf{k}\epsilon}(\mathbf{k}'\rho',\mathbf{k}''\xi'',\mathbf{k}'''\xi''')$ shows that the photon is scattered into the $(\mathbf{k}'\lambda')$ exciton and two phonons, and that H^3, for our model Hamiltonian, does not contain mechanisms leading to the direct second-order Raman effect in the absence of dispersion.

In deriving the expressions for the scattering amplitudes, the nature of the phonons involved has not been specified and, therefore, the results can be used to describe physical processes of either Raman scattering by optical phonons or Brillouin scattering by acoustic phonons. A restriction arises from our model Hamiltonian, which is valid for small wave-vectors only and, hence, second-order effects involving phonons of large but opposite wave-vectors cannot be properly represented by the derived amplitudes. The above derivation of the scattering probabilities does not proceed through perturbation theory and, therefore, the derived results are applicable to the description of the Raman effect under resonance conditions, provided the behaviour of the system and the proper nature of the modes are fully recognized. Numerical calculations of the derived results for real crystals will be necessary for the quantitative comparison with observed data.

VII. Conclusion

The excitation spectrum arising from the interaction of three fields, photon, exciton and phonon in polar crystals has been studied in successive approximations. When anharmonicity is neglected, the spectrum consists of dressed by the phonon field polariton modes, which migrate through the crystal. The exciton-phonon interaction, which is responsible for the dressing of the polariton modes, shifts the dispersion energies that appear in the expression of the dielectric function and produces dispersion in the low energy-phonon part of the spectrum. When anharmonic interactions are taken into account, the absorption bands are found to consist of the superposition of two terms. The first term describes the main Lorentzian line peaked at the renormalized polariton energies, which can be asymmetrically broadened if the energy dependence of the damping function is taken into consideration. The second term describes an asymmetric band, which governs the absorption at frequencies far from the renormalized polariton energies and is responsible for the structure of the side bands. The broadening of the main line comes only from the damping function and it is asymmetric only if the anharmonic interactions are strong enough to make its energy dependence substantial in the narrow frequency range of the order of the line width. On the other hand, the second term contributes over the entire frequency spectrum, except at the renormalized polariton excitation energies, and describes interference effects arising from anharmonic polariton-polariton interactions; it results always in the asymmetric broadening of the main line. The exciton-phonon interaction brings in additional contributions to the damping function and to the interfering term in the expression for the spectral function.

The Stokes components of the first- and second-order Raman scattering amplitudes have been derived in the bare and dressed polariton representation respectively as well as those corresponding to the independent fields. Lattice and excitonic resonance regimes have been considered for both outgoing and incoming modes. In the dressed polariton representation, the resonance energies are shifted with respect to the exciton energy $\bar{E}_{\mathbf{k}\lambda}$ and phonon frequency $\bar{\omega}_{\mathbf{k}\xi}$ respectively. When the exciton-phonon interaction vanishes, these energy shifts disappear and the expression for the polariton scattering probability includes terms that resonate only in the excitonic region of frequencies. The resonating terms have been shown to be the coefficients of the canonical transformation, which diagonalize the first-order Hamiltonian and, therefore, they take the extreme values of zero and unity. Thus resonance does not bring divergence in the scattering amplitudes, but instead a rearrangement of the various terms occurs arising from the fact that electromagnetic content of the polariton mode is reduced to zero. The existence of a resonant enhancement in the expression for the scattering probability cannot be ascertained analytically. The frequency dependence of the Raman amplitude, as well as the excitation spectrum and the line-shape of the absorption bands, have to be computed numerically for an actual crystal.

Appendix

To calculate the two-particle Green functions appearing in the expression for $P_{ij}(\mathbf{k},\omega)$ in the polariton representation, we introduce the row vector operator

$$g_2^\dagger(\mathbf{k}_1,\mathbf{k}_2) = (\gamma_{\rho_1}(\mathbf{k}_1)\,\gamma_{\rho_2}^\dagger(\mathbf{k}_2) \quad \gamma_{\rho_1}(\mathbf{k}_1)\,\gamma_{\rho_2}(\mathbf{k}_2) \quad \gamma_{\rho_1}^\dagger(\mathbf{k}_1)\,\gamma_{\rho_2}^\dagger(\mathbf{k}_2) \quad \gamma_{\rho_1}^\dagger(\mathbf{k}_1)\,\gamma_{\rho_2}^\dagger(\mathbf{k}_2)). \tag{A.1}$$

Using this operator and its hermitian conjugate, we define the two-particle Green function $G_2(\mathbf{k}',\mathbf{k}'',\omega) = \langle\langle g_2(\mathbf{k}',\mathbf{k}'');g_2^\dagger(\mathbf{k}_1,\mathbf{k}_2)\rangle\rangle$, the equation of motion which is given by

$$\omega G(\mathbf{k}'\mathbf{k}'',\omega) = \frac{1}{2\pi}\langle[g_2(\mathbf{k}',\mathbf{k}''),g_2^\dagger(\mathbf{k}_1,\mathbf{k}_2)]_-\rangle_{t=t'} + \langle\langle[g_2(\mathbf{k}'\mathbf{k}''),H_0^{\mathrm{pol}}]_-;g_2^\dagger(\mathbf{k}_1\mathbf{k}_2)\rangle\rangle, \tag{A.2}$$

where the polariton Hamiltonian H_0^{pol} is given by (5.5). From (A.2) we obtain the matrix elements of $G_2(\mathbf{k}',\mathbf{k}'',\omega)$:

$$\langle\langle\gamma_{\rho'}^\dagger(\mathbf{k}')\,\gamma_{\rho''}(\mathbf{k}'');\gamma_{\rho_1}(\mathbf{k}_1)\,\gamma_{\rho_2}^\dagger(\mathbf{k}_2)\rangle\rangle = \left(\frac{1}{2\pi}\right)\cdot\frac{[n_{\rho'}(\mathbf{k}')-n_{\rho''}(\mathbf{k}'')]}{\omega+[\omega_{\rho'}(\mathbf{k}')-\omega_{\rho''}(\mathbf{k}'')]}\,\delta_{\rho'\rho_1}\delta_{\rho''\rho_2}\delta_{\mathbf{k}'\mathbf{k}_1}\delta_{\mathbf{k}''\mathbf{k}_2}, \tag{A.3a}$$

$$\langle\langle\gamma_{\rho'}^\dagger\gamma_{\rho''};\gamma_{\rho_1}^\dagger\gamma_{\rho_2}\rangle\rangle = \left(\frac{1}{2\pi}\right)\cdot\frac{(n_{\rho'}-n_{\rho''})}{\omega+(\omega_{\rho'}-\omega_{\rho''})}\,\delta_{\mathbf{k}',\mathbf{k}_2}\delta_{\mathbf{k}'',\mathbf{k}_1}, \tag{A.3b}$$

$$\langle\langle\gamma_{\rho'}\gamma_{\rho''}^\dagger;\gamma_{\rho_1}^\dagger\gamma_{\rho_2}\rangle\rangle = -\left(\frac{1}{2\pi}\right)\cdot\frac{(n_{\rho'}-n_{\rho''})}{\omega-(\omega_{\rho'}-\omega_{\rho''})}\,\delta_{\mathbf{k}',\mathbf{k}_1}\delta_{\mathbf{k}'',\mathbf{k}_2}, \tag{A.3c}$$

$$\langle\langle\gamma_{\rho'}\gamma_{\rho''}^\dagger;\gamma_{\rho_1}\gamma_{\rho_2}^\dagger\rangle\rangle = -\left(\frac{1}{2\pi}\right)\cdot\frac{(n_{\rho'}-n_{\rho''})}{\omega-(\omega_{\rho'}-\omega_{\rho''})}\,\delta_{\mathbf{k}',\mathbf{k}_2}\delta_{\mathbf{k}'',\mathbf{k}_1}, \tag{A.3d}$$

$$\langle\langle\gamma_{\rho'}^\dagger\gamma_{\rho''}^\dagger;\gamma_{\rho_1}\gamma_{\rho_2}\rangle\rangle = -\left(\frac{1}{\pi}\right)\cdot\frac{(1+n_{\rho'}+n_{\rho''})}{\omega+(\omega_{\rho'}+\omega_{\rho''})}\,(\delta_{\mathbf{k}',\mathbf{k}_1}\delta_{\mathbf{k}'',\mathbf{k}_2}+\delta_{\mathbf{k}',\mathbf{k}_2}\delta_{\mathbf{k}'',\mathbf{k}_1}, \tag{A.3e}$$

$$\langle\langle\gamma_{\rho'}\gamma_{\rho''};\gamma_{\rho_1}^\dagger\gamma_{\rho_2}^\dagger\rangle\rangle = \left(\frac{1}{\pi}\right)\cdot\frac{(1+n_{\rho'}+n_{\rho''})}{\omega-(\omega_{\rho'}+\omega_{\rho''})}\,(\delta_{\mathbf{k}',\mathbf{k}_1}\delta_{\mathbf{k}'',\mathbf{k}_2}+\delta_{\mathbf{k}',\mathbf{k}_2}\delta_{\mathbf{k}'',\mathbf{k}_1}). \tag{A.3f}$$

All the two-particle Green functions appearing in the expression for $P_{ij}(\mathbf{k},\omega)$ consist of a linear combination of (A.3). The average value of the polariton occupation number is denoted by

$$\langle \gamma^{\dagger}_{\rho'}(\mathbf{k}')\,\gamma_{\rho''}(\mathbf{k}'')\rangle = n_{\rho'}(\mathbf{k}')\,\delta_{\rho'\rho''}\delta_{\mathbf{k}',\mathbf{k}''} = n_{\rho'}\delta_{\mathbf{k}',\mathbf{k}''}.$$

In our notation, $\delta_{\mathbf{k}',\mathbf{k}''}$ implies also $\delta_{\rho'\rho''}$ and the $\mathbf{k}$-dependence of the polariton energy $\omega_\rho = \omega_\rho(\mathbf{k})$ has been suppressed, for sake of convenience. The poles of the functions (A.3) are located at the energies $\omega = \pm\omega_{\rho'}(\mathbf{k}') \pm \omega_{\rho''}(\mathbf{k}'')$.

Similarly, for the three-particle Green functions, we introduce the row operator

$$\begin{aligned} g_3^{\dagger}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3) = (&\gamma^{\dagger}_{\rho_1}(\mathbf{k}_1)\,\gamma^{\dagger}_{\rho_2}(\mathbf{k}_2)\,\gamma^{\dagger}_{\rho_3}(\mathbf{k}_3) \quad \gamma_{\rho_1}(\mathbf{k}_1)\,\gamma^{\dagger}_{\rho_2}(\mathbf{k}_2)\,\gamma^{\dagger}_{\rho_3}(\mathbf{k}_3)\\ &\gamma^{\dagger}_{\rho_1}(\mathbf{k}_1)\,\gamma_{\rho_2}(\mathbf{k}_2)\,\gamma^{\dagger}_{\rho_3}(\mathbf{k}_3) \quad \gamma^{\dagger}_{\rho_1}(\mathbf{k}_1)\,\gamma^{\dagger}_{\rho_2}(\mathbf{k}_2)\,\gamma_{\rho_3}(\mathbf{k}_3) \quad \gamma_{\rho_1}(\mathbf{k}_1)\,\gamma_{\rho_2}(\mathbf{k}_2)\,\gamma^{\dagger}_{\rho_3}(\mathbf{k}_3)\\ &\gamma_{\rho_1}(\mathbf{k}_1)\,\gamma^{\dagger}_{\rho_2}(\mathbf{k}_2)\,\gamma_{\rho_3}(\mathbf{k}_3) \quad \gamma^{\dagger}_{\rho_1}(\mathbf{k}_1)\,\gamma_{\rho_2}(\mathbf{k}_2)\,\gamma_{\rho_3}(\mathbf{k}_3) \quad \gamma_{\rho_1}(\mathbf{k}_1)\,\gamma_{\rho_2}(\mathbf{k}_2)\,\gamma_{\rho_3}(\mathbf{k}_3)). \end{aligned} \tag{A.4}$$

From this operator, together with its hermitian conjugate vector operator $g_3(\mathbf{k}',\mathbf{k}'',\mathbf{k}''')$, we define a three-particle Green function $G_3(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\omega)$, whose equation of motion is similar to (A.2). Using the following notation

$$\begin{aligned} \langle \gamma^{\dagger}_{\rho_1}(\mathbf{k}_1)\,\gamma^{\dagger}_{\rho_2}(\mathbf{k}_2)\,\gamma_{\rho_3}(\mathbf{k}_3)\,\gamma_{\rho_4}(\mathbf{k}_4)\rangle &= n_{\rho_1}(\mathbf{k}_1)n_{\rho_2}(\mathbf{k}_2)(\delta_{\mathbf{k}_1,\mathbf{k}_3}\delta_{\mathbf{k}_2,\mathbf{k}_4} + \delta_{\mathbf{k}_1,\mathbf{k}_4}\delta_{\mathbf{k}_2,\mathbf{k}_3}),\\ \Delta(\mathbf{k}'\mathbf{k}'',\mathbf{k}_1\mathbf{k}_2) &= \delta_{\mathbf{k}',\mathbf{k}_1}\delta_{\mathbf{k}'',\mathbf{k}_2} + \delta_{\mathbf{k}',\mathbf{k}_2}\delta_{\mathbf{k}'',\mathbf{k}_1},\\ \Delta(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3) &= \delta_{\mathbf{k}',\mathbf{k}_1}\delta_{\mathbf{k}'',\mathbf{k}_2}\delta_{\mathbf{k}''',\mathbf{k}_3} + \delta_{\mathbf{k}',\mathbf{k}_1}\delta_{\mathbf{k}'',\mathbf{k}_3}\delta_{\mathbf{k}''',\mathbf{k}_2} + \ldots 4 \text{ terms}, \end{aligned} \tag{A.5}$$

we can write the twenty non-zero matrix elements of $G_3(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\omega)$:

$$\begin{aligned} G_3^{11}(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\omega) &= \langle\langle \gamma_{\rho'}\gamma_{\rho''}\gamma_{\rho'''};\gamma^{\dagger}_{\rho_1}\gamma^{\dagger}_{\rho_2}\gamma^{\dagger}_{\rho_3}\rangle\rangle\\ &= \left(\frac{1}{2\pi}\right)\cdot\frac{[(1+n_{\rho'})(1+n_{\rho''}+n_{\rho'''})+n_{\rho''}n_{\rho'''}]}{\omega-(\omega_{\rho'}+\omega_{\rho''}+\omega_{\rho'''})}\,\Delta(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3) \end{aligned} \tag{A.6a}$$

$$\begin{aligned} G_3^{88}(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\omega) &= \langle\langle \gamma^{\dagger}_{\rho'}\gamma^{\dagger}_{\rho''}\gamma^{\dagger}_{\rho'''};\gamma_{\rho_1}\gamma_{\rho_2}\gamma_{\rho_3}\rangle\rangle\\ &= -\left(\frac{1}{2\pi}\right)\cdot\frac{(1+n_{\rho'})(1+n_{\rho''}+n_{\rho'''})+n_{\rho''}+n_{\rho'''}}{\omega+(\omega_{\rho'}+\omega_{\rho''}+\omega_{\rho'''})}\,\Delta(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3) \end{aligned} \tag{A.6b}$$

$$\begin{aligned} G_3^{22}(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\omega) = \left(\frac{1}{2\pi}\right)\cdot\frac{1}{\omega-(-\omega_{\rho'}+\omega_{\rho''}+\omega_{\rho'''})}\{&[n_{\rho'}(1+n_{\rho''}+n_{\rho'''})\\ &-n_{\rho''}n_{\rho'''}]\delta_{\mathbf{k}',\mathbf{k}_1}\Delta(\mathbf{k}''\mathbf{k}''',\mathbf{k}_2\mathbf{k}_3)+n_{\rho'}\delta_{\mathbf{k}',\mathbf{k}''}[(1+n_{\rho_1})\,\delta_{\mathbf{k}_1,\mathbf{k}_2}\delta_{\mathbf{k}''',\mathbf{k}_3}\\ &+(1+n_{\rho_3})\,\delta_{\mathbf{k}_1,\mathbf{k}_3}\delta_{\mathbf{k}''',\mathbf{k}_2}]+n_{\rho'''}\delta_{\mathbf{k}',\mathbf{k}'''}[(1+n_{\rho_1})\,\delta_{\mathbf{k}_1,\mathbf{k}_2}\delta_{\mathbf{k}'',\mathbf{k}_3}\\ &+(1+n_{\rho_3})\,\delta_{\mathbf{k}_1,\mathbf{k}_3}\delta_{\mathbf{k}'',\mathbf{k}_2}]\} \end{aligned} \tag{A.6c}$$

$$\begin{aligned} G_3^{23}(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\omega) = \left(\frac{1}{2\pi}\right)\left[\frac{1}{\omega-(-\omega_{\rho'}+\omega_{\rho''}+\omega_{\rho'''})}\right]\{&[n_{\rho'}(1+n_{\rho''}+n_{\rho'''})\\ &-n_{\rho''}n_{\rho'''}]\,\delta_{\mathbf{k}',\mathbf{k}_2}\Delta(\mathbf{k}''\mathbf{k}''',\mathbf{k}_1\mathbf{k}_3)\;+n_{\rho'}\delta_{\mathbf{k}',\mathbf{k}''}[n_{\rho_1}\delta_{\mathbf{k}_1,\mathbf{k}_2}\delta_{\mathbf{k}'''\mathbf{k}_3}\\ &+(1+n_{\rho_2})\,\delta_{\mathbf{k}_2,\mathbf{k}_3}\delta_{\mathbf{k}''',\mathbf{k}_1}]\;+n_{\rho'''}\delta_{\mathbf{k}',\mathbf{k}'''}[n_{\rho_1}\delta_{\mathbf{k}_1,\mathbf{k}_2}\delta_{\mathbf{k}'',\mathbf{k}_3}\\ &+(1+n_{\rho_2})\,\delta_{\mathbf{k}_2,\mathbf{k}_3}\delta_{\mathbf{k}'',\mathbf{k}_1}]\} \end{aligned} \tag{A.6d}$$

$$G_3^{24}(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\omega)=\left(\frac{1}{2\pi}\right)\left[\frac{1}{\omega-(-\omega_{\rho'}+\omega_{\rho''}+\omega_{\rho'''})}\right]\{[n_{\rho'}(1+n_{\rho''}+n_{\rho'''})$$
$$-n_{\rho''}n_{\rho'''}]\,\delta_{\mathbf{k}',\mathbf{k}_3}\Delta(\mathbf{k}''\mathbf{k}''',\mathbf{k}_1\,\mathbf{k}_2)\;+n_{\rho'}\delta_{\mathbf{k}',\mathbf{k}''}[n_{\rho_3}\delta_{\mathbf{k}_1,\mathbf{k}_3}\delta_{\mathbf{k}''',\mathbf{k}_2}$$
$$+n_{\rho_2}\delta_{\mathbf{k}_2,\mathbf{k}_3}\delta_{\mathbf{k}'''\mathbf{k}_1}]\;+n_{\rho'''}\delta_{\mathbf{k}',\mathbf{k}'''}[n_{\rho_3}\delta_{\mathbf{k}_1,\mathbf{k}_3}\delta_{\mathbf{k}'',\mathbf{k}_2}+n_{\rho_2}\delta_{\mathbf{k}_2,\mathbf{k}_3}\delta_{\mathbf{k}'',\mathbf{k}_1}]\}\tag{A.6e}$$

$$G_3^{32}(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\omega)=\left(\frac{1}{2\pi}\right)\left[\frac{1}{\omega-(\omega_{\rho'}-\omega_{\rho''}+\omega_{\rho'''})}\right]\{[n_{\rho''}(1+n_{\rho'}+n_{\rho'''})$$
$$-n_{\rho'}n_{\rho'''}]\,\delta_{\mathbf{k}'',\mathbf{k}_1}\Delta(\mathbf{k}'\mathbf{k}''',\mathbf{k}_2\,\mathbf{k}_3)\;+(1+n_{\rho'})\,\delta_{\mathbf{k}',\mathbf{k}''}[(1+n_{\rho_1})\delta_{\mathbf{k}_1,\mathbf{k}_2}\delta_{\mathbf{k}''',\mathbf{k}_3}$$
$$+(1+n_{\rho_3})\,\delta_{\mathbf{k}_1,\mathbf{k}_3}\delta_{\mathbf{k}''',\mathbf{k}_2}]\;+n_{\rho''}\delta_{\mathbf{k}'',\mathbf{k}'''}[(1+n_{\rho_1})\,\delta_{\mathbf{k}_1,\mathbf{k}_2}\delta_{\mathbf{k}',\mathbf{k}_3}$$
$$+(1+n_{\rho_3})\,\delta_{\mathbf{k}_1,\mathbf{k}_3}\delta_{\mathbf{k}',\mathbf{k}_2}]\}\tag{A.6f}$$

$$G_3^{33}(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\omega)=\left(\frac{1}{2\pi}\right)\left[\frac{1}{\omega-(\omega_{\rho'}-\omega_{\rho''}+\omega_{\rho'''})}\right]\{[n_{\rho''}(1+n_{\rho'}+n_{\rho'''})$$
$$-n_{\rho'}n_{\rho'''}]\,\delta_{\mathbf{k}'',\mathbf{k}_2}\Delta(\mathbf{k}'\mathbf{k}''',\mathbf{k}_1\,\mathbf{k}_3)\;+(1+n_{\rho'})\,\delta_{\mathbf{k}',\mathbf{k}''}[(1+n_{\rho_2})\delta_{\mathbf{k}_2,\mathbf{k}_3}\delta_{\mathbf{k}''',\mathbf{k}_1}$$
$$+n_{\rho_1}\delta_{\mathbf{k}_1,\mathbf{k}_2}\delta_{\mathbf{k}''',\mathbf{k}_3}]+n_{\rho''}\delta_{\mathbf{k}'',\mathbf{k}'''}[(1+n_{\rho_2})\delta_{\mathbf{k}_2,\mathbf{k}_3}\delta_{\mathbf{k}',\mathbf{k}_1}+n_{\rho_1}\delta_{\mathbf{k}_1,\mathbf{k}_2}\delta_{\mathbf{k}',\mathbf{k}_3}]\}\tag{A.6g}$$

$$G_3^{34}(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\omega)=\left(\frac{1}{2\pi}\right)\left[\frac{1}{\omega-(\omega_{\rho'}-\omega_{\rho''}+\omega_{\rho'''})}\right]\{[n_{\rho''}(1+n_{\rho'}+n_{\rho'''})$$
$$-n_{\rho'}n_{\rho'''}]\,\delta_{\mathbf{k}'',\mathbf{k}_3}\Delta(\mathbf{k}'\mathbf{k}''',\mathbf{k}_1\,\mathbf{k}_2)\;+(1+n_{\rho'})\,\delta_{\mathbf{k}',\mathbf{k}''}[n_{\rho_3}\delta_{\mathbf{k}_1,\mathbf{k}_3}\delta_{\mathbf{k}''',\mathbf{k}_2}$$
$$+n_{\rho_2}\delta_{\mathbf{k}_2,\mathbf{k}_3}\delta_{\mathbf{k}''',\mathbf{k}_3}]+n_{\rho''}\delta_{\mathbf{k}'',\mathbf{k}'''}[n_{\rho_3}\delta_{\mathbf{k}_1,\mathbf{k}_3}\delta_{\mathbf{k}',\mathbf{k}_2}+n_{\rho_2}\delta_{\mathbf{k}_2,\mathbf{k}_3}\delta_{\mathbf{k}',\mathbf{k}_1}]\}\tag{A.6h}$$

$$G_3^{42}(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\omega)=\left(\frac{1}{2\pi}\right)\left[\frac{1}{\omega-(\omega_{\rho'}+\omega_{\rho''}-\omega_{\rho'''})}\right]\{[n_{\rho'''}(1+n_{\rho'}+n_{\rho''})$$
$$-n_{\rho'}n_{\rho''}]\,\delta_{\mathbf{k}''',\mathbf{k}_1}\Delta(\mathbf{k}'\mathbf{k}'',\mathbf{k}_2\,\mathbf{k}_3)+(1+n_{\rho'''})\,\delta_{\mathbf{k}',\mathbf{k}'''}[(1+n_{\rho_1})\,\delta_{\mathbf{k}_1,\mathbf{k}_2}\delta_{\mathbf{k}'',\mathbf{k}_3}$$
$$+(1+n_{\rho_3})\,\delta_{\mathbf{k}_1,\mathbf{k}_3}\delta_{\mathbf{k}'',\mathbf{k}_2}]+(1+n_{\rho''})\,\delta_{\mathbf{k}'',\mathbf{k}'''}[(1+n_{\rho_1})\,\delta_{\mathbf{k}_1,\mathbf{k}_2}\delta_{\mathbf{k}',\mathbf{k}_3}$$
$$+(1+n_{\rho_3})\,\delta_{\mathbf{k}_1,\mathbf{k}_3}\delta_{\mathbf{k}',\mathbf{k}_2}]\}\tag{A.6i}$$

$$G_3^{43}(\mathbf{k}'\mathbf{k}''\mathbf{k}''',\omega)=\left(\frac{1}{2\pi}\right)\left[\frac{1}{\omega-(\omega_{\rho'}+\omega_{\rho''}-\omega_{\rho'''})}\right]\{[n_{\rho'''}(1+n_{\rho'}+n_{\rho''})$$
$$-n_{\rho'}n_{\rho''}]\,\delta_{\mathbf{k}''',\mathbf{k}_2}\Delta(\mathbf{k}'\mathbf{k}'',\mathbf{k}_1\,\mathbf{k}_3)+(1+n_{\rho'''})\,\delta_{\mathbf{k}'\mathbf{k}'''}[n_{\rho_1}\delta_{\mathbf{k}_1,\mathbf{k}_2}\delta_{\mathbf{k}'',\mathbf{k}_3}$$
$$+(1+n_{\rho_2})\,\delta_{\mathbf{k}_2,\mathbf{k}_3}\delta_{\mathbf{k}'',\mathbf{k}_1}]+(1+n_{\rho''})\,\delta_{\mathbf{k}'',\mathbf{k}'''}[n_{\rho_1}\delta_{\mathbf{k}_1,\mathbf{k}_2}\delta_{\mathbf{k}',\mathbf{k}_3}$$
$$+(1+n_{\rho_2})\,\delta_{\mathbf{k}_2,\mathbf{k}_3}\delta_{\mathbf{k}',\mathbf{k}_1}]\tag{A.6k}$$

$$G_3^{44}(\mathbf{k}'\mathbf{k}''\mathbf{k}''', \omega) = \left(\frac{1}{2\pi}\right)\left[\frac{1}{\omega - (\omega_{\rho'} + \omega_{\rho''} - \omega_{\rho'''})}\right]\{[n_{\rho'''}(1 + n_{\rho'} + n_{\rho''})$$
$$- n_{\rho'} n_{\rho''}]\, \delta_{\mathbf{k}''',\mathbf{k}_3} \Delta(\mathbf{k}'\mathbf{k}'', \mathbf{k}_1\mathbf{k}_2) + (1 + n_{\rho'})\, \delta_{\mathbf{k}',\mathbf{k}'''}[n_{\rho_3} \delta_{\mathbf{k}_1,\mathbf{k}_3} \delta_{\mathbf{k}'',\mathbf{k}_2}$$
$$+ n_{\rho_2} \delta_{\mathbf{k}_2,\mathbf{k}_3} \delta_{\mathbf{k}'',\mathbf{k}_1}] + (1 + n_{\rho''})\, \delta_{\mathbf{k}'',\mathbf{k}'''}[n_{\rho_3} \delta_{\mathbf{k}_1,\mathbf{k}_3} \delta_{\mathbf{k}',\mathbf{k}_2} + n_{\rho_2} \delta_{\mathbf{k}_2,\mathbf{k}_3} \delta_{\mathbf{k}',\mathbf{k}_1}]\} \tag{A.6 l}$$

The other matrix elements $G_3^{ij}(\mathbf{k}'\mathbf{k}''\mathbf{k}''', \omega)$ are obtained from the above expressions in the following way: a) permutation of the indices ij according to the scheme $1 \leftrightarrow 8$, $2 \leftrightarrow 7$, $3 \leftrightarrow 6$ and $4 \leftrightarrow 5$; b) the sign of the functions (A.6) is reversed as well as the sign of the linear combination ω_ρ in the denominator; c) in the second and third terms of the numerator, $n_{\rho_i} \delta_{\mathbf{k}_i,\mathbf{k}_j} \leftrightarrow (1 + n_{\rho_i})\, \delta_{\mathbf{k}_i,\mathbf{k}_j}$ for $i, j = 1, 2, 3$ and $i, j = {}', {}'', {}'''$.

By combining linearly the $G_3^{ij}(\mathbf{k}'\mathbf{k}''\mathbf{k}''', \omega)$, we get all the three-particle Green functions contained in $P_3^{ij}(\mathbf{k}, \omega)$. In doing such a combination, one must keep in mind that

$$G_n(\mathbf{k}\ldots, \omega) = G_n(\mathbf{k}\ldots, -\omega) \tag{A.7}$$

in the complex ω-plane for both two- and three-particle Green functions. The poles of the functions (A.6) are located at the energies $\pm\omega_{\rho'} \pm \omega_{\rho''} \pm \omega_{\rho'''}$.

Using the functions (A.3) and (A.6), the matrix elements $P_{ij}(\mathbf{k}, \omega)$ of the scattering operator (3.9), which are linear combinations of two- and three-particles Green functions, can be written in the general form:

$$P_{ij}(\mathbf{k}, \omega) = \sum_{\substack{\mathbf{k}'\mathbf{k}'' \\ \rho'\rho''}} \left\{ \frac{(1 + n_{\rho'} + n_{\rho''})}{\omega^2 - (\omega_{\rho'} + \omega_{\rho''})^2} [(\omega_{\rho'} + \omega_{\rho''})\, \Gamma^{s}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}''\rho'') + \omega \hat{\Gamma}^{s}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}''\rho'')] \right.$$
$$\left. - \frac{(n_{\rho'} - n_{\rho''})}{\omega^2 - (\omega_{\rho'} - \omega_{\rho''})^2} [(\omega_{\rho'} - \omega_{\rho''})\, \Gamma^{AS}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}''\rho'') + \omega \hat{\Gamma}^{AS}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}''\rho'')] \right\}$$
$$\times \delta_{\mathbf{k}'-\mathbf{k}'',\mathbf{k}} + \sum_{\substack{\mathbf{k}'\mathbf{k}''\mathbf{k}''' \\ \rho'\rho''\rho'''}} \left\{ \frac{(1 + n_{\rho'} + n_{\rho''} + n_{\rho'''} + n_{\rho'} n_{\rho''} + n_{\rho''} n_{\rho'''} + n_{\rho'''} n_{\rho'})}{\omega^2 - (\omega_{\rho'} + \omega_{\rho''} + \omega_{\rho'''})^2} \right.$$
$$\times [(\omega_{\rho'} + \omega_{\rho''} + \omega_{\rho'''})\, \Gamma^{s}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}''\rho'', \mathbf{k}'''\rho''') + \omega \hat{\Gamma}^{s}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}''\rho'', \mathbf{k}'''\rho''')]$$
$$+ \frac{[n_{\rho'}(1 + n_{\rho''} + n_{\rho'''}) - n_{\rho''} n_{\rho'''}]}{\omega^2 - (-\omega_{\rho'} + \omega_{\rho''} + \omega_{\rho'''})^2} [(-\omega_{\rho'} + \omega_{\rho''} + \omega_{\rho'''})\, \Gamma^{T1}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}''\rho'', \mathbf{k}'''\rho''')$$
$$+ \omega \hat{\Gamma}^{T1}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}''\rho'', \mathbf{k}'''\rho''')] + \frac{[n_{\rho''}(1 + n_{\rho'} + n_{\rho'''}) - n_{\rho'} n_{\rho'''}]}{\omega^2 - (\omega_{\rho'} - \omega_{\rho''} + \omega_{\rho'''})^2}$$
$$\times [(\omega_{\rho'} - \omega_{\rho''} + \omega_{\rho'''})\, \Gamma^{T2}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}''\rho'', \mathbf{k}'''\rho''') + \omega \hat{\Gamma}^{T2}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}''\rho'', \mathbf{k}'''\rho''')]$$
$$+ \frac{[n_{\rho'''}(1 + n_{\rho'} + n_{\rho''}) - n_{\rho'} n_{\rho''}]}{\omega^2 - (\omega_{\rho'} + \omega_{\rho''} - \omega_{\rho'''})^2} [(\omega_{\rho'} + \omega_{\rho''} - \omega_{\rho'''})\, \Gamma^{T3}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}''\rho'', \mathbf{k}'''\rho''')$$

$$
\left. + \omega \hat{\Gamma}^{T3}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}''\rho'', \mathbf{k}'''\rho''')] \right\} \delta_{\mathbf{k}'\pm\mathbf{k}''\pm\mathbf{k}''',\mathbf{k}} + \sum_{\substack{\mathbf{k}'\mathbf{k}''\mathbf{k}''' \\ \rho'\rho''\rho'''}} \left\{ \frac{1}{(\omega^2 - \omega^2_{\rho'})} \right.
$$

$$
\times [\omega_{\rho'} R^{T1}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}''\rho'') + \omega \hat{R}^{T1}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}''\rho'')] + \frac{1}{(\omega^2 - \omega^2_{\rho''})}
$$

$$
\times [\omega_{\rho''} R^{T2}_{\mathbf{k}\alpha}(\mathbf{k}''\rho'', \mathbf{k}'''\rho''') + \omega \hat{R}^{T2}_{\mathbf{k}\alpha}(\mathbf{k}''\rho'', \mathbf{k}'''\rho''')] + \frac{1}{(\omega^2 - \omega^2_{\rho'''})}
$$

$$
\left. \times [\omega_{\rho'''} R^{T3}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}'''\rho''') + \omega \hat{R}^{T3}_{\mathbf{k}\alpha}(\mathbf{k}'\rho', \mathbf{k}'''\rho''')] \right\} \delta_{\mathbf{k}'\pm\mathbf{k}''\pm\mathbf{k}''',\mathbf{k}}. \tag{A.8}
$$

In (A.8) the index α stands for the polarization indices ϵ, λ and ξ of the incoming mode The first term in (A.8), which is summed over the two outgoing polaritons, represents first-order scattering process, the Stokes component is proportional to $(1 + n_{\rho'} + n_{\rho''})$, whereas that of the anti-Stokes is proportional to $(n_{\rho'} - n_{\rho''})$. In the second term, the summation runs over the three outgoing modes and corresponds to the second-order scattering process. The last term results from the last two terms in the numerator of the three-particle Green functions (A.6) and represents scattering events, where two of the outgoing modes have the same band index ρ and wave-vector $\mathbf{k}$ and cancel each other.

Making use of the relation (A.7), it is found that in the expressions for $P_{22}(\mathbf{k}, \omega)$ and $P_{33}(\mathbf{k}, \omega)$, all coefficients $\hat{\Gamma}$ and $\hat{R}$ vanish, whereas they are non-zero but can be, nevertheless, neglected for $P_{11}(\mathbf{k}, \omega)$ and $P_{14}(\mathbf{k}, \omega)$. All the coefficients in (A.8) are easily expressed in terms of the anharmonic coupling constants and the u's and v's for the outgoing modes. The algebra involved is rather tedious and the final expressions are so lengthy that they will not be given here.

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